

CHEMISTRY

BOOKS - IIT-JEE PREVIOUS YEAR (CHEMISTRY)

ALKYL HALIDES

lee Main And Advanced

1. The increasing order of reactivity of the following halides

for the $S_N 1$ reaction is

 $I.CH_3CH(CI)CH_2CH_3$

 $II. CH_3CH_2CH_2Cl$

III. p. $-H_3CO-C_6H_4-CH_2Cl$

$$\mathsf{A.}\left(II\right)<\left(II\right)<\left(I\right)$$

$$\mathsf{B.}\left(II\right)<\left(I\right)<\left(III\right)$$

$$\mathsf{D.}\left(II\right)<\left(III\right)<\left(I\right)$$

Answer: B



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

A.

C

Answer: A



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3. 3-menthyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is

A. six

- B. zero
- C. two
- D. four

Answer: D



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4. The major product obtained in the following reaction is

$$C_6H_5$$
 C_6H_5
 C_6H_5
 C_6H_5

A.
$$(\pm)C_6H_5CHig(O^tBuig)CH_2C_6H_5$$

$$\mathsf{B.}\, C_6H_5CH=CHC_6H_5$$

C.
$$(+)C_6H_5CHig(O^tBuig)CH_2C_6H_5$$

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

Answer: B



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5. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields:

(a)
$$C_2H_5CH_2 \overset{|C|}{\underset{CH_3}{C}} - OCH_3$$
 (b) $C_2H_5CH_2 \overset{|C|}{\underset{CH_3}{C}} = CH_2$ (c) $C_2H_5CH_2 = \overset{|C|}{\underset{CH_3}{C}} - CH_3$

A. Both I and III

 CH_{3}

B. only III

C. Both I and II

D. All of these

Answer: D



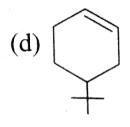
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6. The product of the reaction gives below is:

$$\xrightarrow{1. \text{ NBS/hv}} X$$

В.

C



D.

Answer: A



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7. The synthesis of alkyl fluoride is best accomplished by:

A. free radical fluorination

B. Sandmeyer's reaction

C. Finkelstein reaction

D. Swarts reaction

Answer: D



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8. In $S_N 2$ reactions, the correct order of reactivity for the following compounds:

 $CH_3CI, CH_3CH_2CI, (CH_3)_2CHCI$ and $(CH_3)_2CCI$ is:

A.

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

В.

 $CH_{3}Cl > CH_{3}CH_{2}Cl > (CH_{3})_{2}CHCl > (CH_{3})_{3}CCl$

C.

 $CH_3CH_2Cl>CH_3Cl>(CH_3)_2CHCl>(CH_3)_2CCl$

D.

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

Answer: B



9. Match the chemical conversion in List-I with the approprotae reagents in List-II and select the correct

answer using the code given below this list-

Liet-II (P) (I) (I) Hg(OAc]₂ (II) NaBH₄ ((J) ONa OEt (2) NaOEt (P) OH (II) BH₃ (II) H₂O₂ /NaOH

 $\begin{array}{ccccc} P & Q & R & S \\ \text{B. 3} & 2 & 1 & 4 \end{array}$

 $egin{array}{cccccc} P & Q & R & S \\ {\sf C.} & 2 & 3 & 4 & 1 \end{array}$

Answer: A



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10. KI in acetone, undergoes $S_N 2$ reaction with each of

 $P,\,Q,\,R$ and S The rates of the reaction very as

$$H_3C_P-Cl$$
 Q R S

•

$$\operatorname{A.}P>Q>R>S$$

$$\operatorname{B.}S>P>R>Q$$

$$\mathsf{C}.\,P>R>Q>S$$

$$\operatorname{D.}R>P>S>Q$$

Answer: B



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11. The major product of the following reaction is

A.

Β.

C.

D.

Answer: A



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12. The following compound on hydrolysis in equeous acetone will give .

A. k and L

B. only K

C. L and M

D. only M

Answer: A



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13. The product of following reaction is

$$OH + C_2H_5I \xrightarrow{C_2H_5O^-} anhy. C_2H_5OH$$

A.
$$C_6H_5OC_2H_5$$

B.
$$C_2H_5OC_2H_5$$

$$\mathsf{C.}\ C_6H_5OC_6H_5$$

D.
$$C_6H_5l$$

Answer: A



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14. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformations.

$$CH_3-CH_2CH_2Br \stackrel{X}{\longrightarrow} Product \stackrel{Y}{\longrightarrow}$$

$$CH_3 - CH - CH_3$$

Br

A. X=dilute aqueous

 $NaOH, 20^{\circ}, Y = HBr / \text{acetic acid}, 20^{\circ}C$

B. X=concentrated alcoholic $NaOH,\,80^{\circ}\,C,$,

Y=HBr//acetic acid, 20[^](@)C[^]

 $\mathsf{C}.\,X = dilute a que ous$

NaOH,20[^](@)C,Y=Br (2)//CHCl (3), 0[^](@)

 ${\sf D}.\,X=concentrate daqueous {\sf NaOH}, \hspace{1cm} {\sf 80^(@)C},$

=Br_(2)//CHCl_(3),)^(@)C`

Answer: B



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15. The compound that will react most readily with NaOH to from methanol is

A.
$$(CH_3)_4N^+l^-$$

B. CH_3OCH_3

C. $(CH_3)_3 S^+ l^-$

D. $(CH_3)_3Cl$

Answer: A



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16. An SN^2 reaction of an asymmetric carbon of a compound always gives :

A. an enanatiomer of the substrate

B. a product with opposite optical ratation

C. a mixture of diastereomers

D. a single stereoisomer

Answer: D



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17. The order of reactivities of the following alky halides for an ${\cal S}_N 2$ reaction is .

A.
$$RF > RCl > RBr > Rl$$

$$\mathrm{B.}\,RF>RBr>RCl>Rl$$

$$\mathsf{C}.\,RCl>RBr>RF>Rl$$

$$extsf{D}. \, Rl > RBr > RCl > RF$$

Answer: D



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18. Which of the following has the highest nucleophilicity

B.
$$OH^-$$

$$\mathsf{C.}\,CH_3^-$$

$$\operatorname{D.} NH_2^{\,-}$$

Answer: C



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19. A solution of (+)2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCI_5$ due to the formation of-

- A. carbanion
- B. carbene
- C. free-radical
- D. carbocation

Answer: D



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20. Which of the following is an organometallic compound?

A. Lithium mehtoxide

- B. Lithium acetate
- C. Lithium dimethylamide
- D. Methyl lithium

Answer: D



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21. $(CH_3)_3CMgCl$ on reaction with D_2O produces

- A. $(CH_3)_3CD$
- $\operatorname{B.}(CH_3)_3COD$
- $\mathsf{C}.\,(CD)_3CD$
- $\operatorname{D.}(CD)_3COD$

Answer: A



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22. With alcoholic potash, $C_4H_8Cl_2$ (A) gives C_4H_6 (B), which reacts with ammoniacal cuprous chloride. Identify the compounds (A) and (B).

- A. 1-butene
- B. 1-butanol
- C. 2-butene
- D. 2-butanol

Answer: A



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23. n-Propyl bromide on treatment with ethanolic potassium hydroxide produes .

- A. propane
- B. propene
- C. propyne
- D. propanol

Answer: B



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24. The reaction conditions leading to the best yield of C_2H_5Cl are

A.
$$C_2H_6(ext{excess})+cl_2 \stackrel{ ext{UV light}}{\longrightarrow}$$

B.
$$C_2H_6+cl_2(ext{excess}) \xrightarrow[ext{room temp.}]{ ext{dark}}$$

C.
$$C_2H_6+Cl_2(ext{excess})\stackrel{ ext{UV light}}{\longrightarrow}$$

D.
$$C_2H_6+Cl_2\stackrel{ ext{UV light}}{\longrightarrow}$$

Answer: A



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25. For the following compounds, the correct statement (s) with respect to nuclephilic substitution reaction is (are)

A. Compound IV undergoes inversion of configuration

B. The order of reactivity for I , III and IV is :

C. I and III follow $S_N l$ mechanism

D. I and II follow $S_N l$ mechanism

Answer: A::B



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26. Compound (S) that on hydrogenation product (S) optically inactive compound (s) is/are

Answer: B::D



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27. In the following reaction, the major product is

$$CH_3$$
 CH_2
1 equivalent HBr

$$\begin{array}{c} \text{(a)}_{\text{H}_2\text{C}} & \text{CH}_3 \\ \text{Br} & \text{CH}_5 \end{array}$$

D.
$$(d)_{H_3C}$$
 $(d)_{Br}$

Answer: D



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28. The compound(s) used as refrigerant are

A. NH_3

B. CCl_4

 $\mathsf{C.}\,CF_4$

D. CF_2Cl_2

Answer: A::D



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29. Match the following:

	Column I		Column II
A.	$\mathrm{CH_3}$ — CHBr — $\mathrm{CD_3}$ on treatment with alc. KOH gives $\mathrm{CH_2}$ = CH — $\mathrm{CD_3}$ as a major product.	p.	E1 reaction
В.	Ph—CHBr—CH $_3$ reacts faster than Ph—CHBr—CD $_3$	q.	E2 reaction
C.	Ph— CH_2 — CH_2Br on treatment with C_2H_5 OD/C_2H_5 O^- gives Ph— CD — CH_2 as the major product.	r.	E1CB reaction
D.	PhCH ₂ CH ₂ Br and PhCD ₂ CH ₂ Br react with same rate.	S.	First order reaction



30. Vinyl chloride on reaction with the dimethyl copper gives......



31. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with



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32. The halogen which is most reactions, in the halogenation of alkanes under sunlight is



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33. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methyl propane in the ratio 9:1.



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34. During SN^1 reactions, the leaving group leaves the molecule before the incoming group is attached to the molecule. Explain



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35. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule.



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36. Iodide is a better nucleophile than bromide.Explain



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37. Carbon tetrachloride is inflammable.



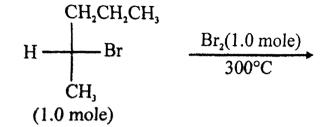
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38. Carbon tetrachloride burns in air when lighted ti give phosgene.



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39. In the following monobromination reaction, the number of possible chiral products is





40. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is



41. Identify X,Y and Z in the following synsthetic scheme and write their structures

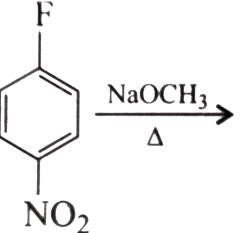
 $X \xrightarrow{H_2 \, / \, pd \, - \, BaSO_4} Y \xrightarrow{ ext{alkaline}} Z$

 $CH_{3}CH_{2}C=CH \xrightarrow[(ii)CH_{3}CH_{2}Br]{(ii)CH_{3}CH_{2}Br} X$

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42. What would be that major product in each of the following reactions?

i.
$$CH_3 - CH_3 - CH_2 Br \xrightarrow[CH_3]{C} CH_3$$





ii.

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43. Write the structures of the products:

$$C_6H_5CH_2CHClC_6H_5 \xrightarrow{ ext{Alc.KOH}}$$



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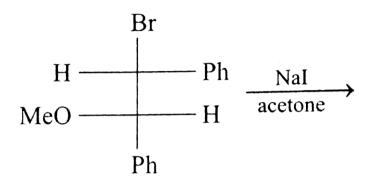
44. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?

- i. $(CH_3)_3CBr+NaOMe
 ightarrow$
- ii. $CH_3Br + NaO t Bu
 ightarrow$



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45. Predict the structure of the product in the following reaction

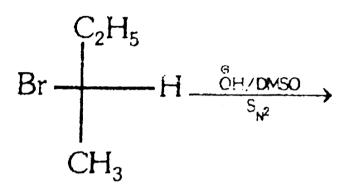




46. Optically active 2-iodo butane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly.



47. Draw the stereochemical structure of the product in the following reaction.



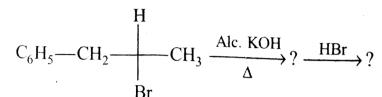


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48. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alyl halides due to



49. Identify the major product in the following reaction.





(i)

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50. Write the structures of the major organic product expected from each of the following reactions :

(i)
$$H_3C$$
 CH_2CH_3 $Alc. KOH$ Cl

(ii)
$$CH_3CH_2CHCl_2 \xrightarrow{aq. alkalibooil}$$

(ii)
$$CH_3CH_2CHCl_2 \xrightarrow[\mathrm{boil}]{\mathrm{aq.alkali}}$$

- **51.** Arrange the following in order of their
- (i) Increasing basicity

$$H_2O$$
, OH^- , CH_3OH , CH_3O^-

(ii) Increasing reactivity in nucleophilic substitution reactions

 CH_3F , CH_3l , CH_3Br , CH_3Cl



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52. Chloroform is stored in dark coloured bottles. Explain in not more than two sentences.



53. Show by chemical equations only, how would you prepare the following from the indicated starting materials ? Specify the reagents in each step of the synthesis.

- (i) Chloroform from carbon disulphide.
- (ii) Hexachloroethane (C_2Cl_6) from calcium carbide.



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54. Arrange the following compounds in decreasing order of number of alkene isomers that could be produced by the reaction of each of the following with boiling solution of ethanolic KOH

- I. 1-bromobutane
- II. 3-bromopentane

III. 3-bromo-3-methylpentane

IV. 3-bromohexane

A.
$$I>II>III>IV$$

$$\mathrm{B.}\,IV > III > I > II$$

$$\mathsf{C}.\,IV > III > II > I$$

$$\mathsf{D}.\,III > IV > II > I$$

Answer: C



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55. For the follwing isomeric chlorides, what will be the increasing order of reactivity in $S_N 2$ reaction ?

I. 4-chlorobutene

II. 1-chlorobutene

(iii) 1-chloro-2- butene

2-chlorobutene

A.
$$IV < II < I < III$$

$$\mathrm{B.}\,IV < II < III < I$$

$$\mathsf{C}.\,II < IV < III < I$$

D.
$$II < IV < I < III$$

Answer: A



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56. $AC_6H_{14}O$ chiral alcohol is converted to a bromide by treatment with PBr_3 . Reaction of this bromide, first with

Mg in ether , followed by quenching in 0.1NHCl produces an achiral C_6H_{14} hydrocarbon. Which of the following is the original alcohol?

- A. 2-ethyl-1-butanol
- B. 4-methyl-1-pentanol
- C. 3-methyl-3-pentanol
- D. 3-methyl-1-pentanol

Answer: D



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57. Consider the S_N1 solvolysis of the following 1° -alkyl chlorides in aqueous ethanol.

I. $CH_3CH_2CH_2Cl$

II. $CH_2 = CHCH_2Cl$

III. CH_3OCH_2Cl

iv. $CF_3CF_2CH_2Cl$

What is the order of decreasing reactivity?

A. III > II > I > IV

B. II > I > III > IV

 $\mathsf{C}.\,IV > III > II > I$

D. I > II > III > Iv

Answer: C



58. In the S_N2 reaction of iodide ion with $(CH_3)_2CHCH_2CH_2X$, what is the order of decreasing reactivity for the following X substituents ?

I.
$$X = -OH$$
 , II. $X = CH_3CO_2^-$

III
$$X = CF_3SO_3^-$$
 ,IV. $X = \mathbb{C}l_3CO_2^-$

A.
$$I > II > III > IV$$

C.
$$III > II > IV > I$$

D.
$$III > IV > II > I$$

Answer: D



59. The nucleophile producing functional isomers on reaction with \underline{n} - butyl bromide

A. NaCN

B. NaSCN

C. $NaNO_3$

D. NaOCN

Answer: A::B::D



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60. Reaction of 1,4 - dibromobutane with Mg turnings in ether gives the bis-Grignard's reagent, $BrMgCH_2CH_2CH_2CH_2MgBr \ . \ \ \ What \ \ is \ \ the \ \ product$

from the reaction of meso-2,3-dibromobutane with Mg under the same conditions?

A. Trans-2-butene

B. Cis-2-butene

 ${\sf C.}\ Meso-CH_3CH(MgBr)CH(MgBr)CH_3$

D. Recemic $-CH_3CH(MgBr)CH(MgBr)CH_3$

Answer: A::C



61. The $S_N 2$ reaction of 1-chloro-3-methylbutane with sodium methoxide is relatively slow , but can be

accelerated by the addition of a small amount of Nal . How is this catalysis best explained ?

A. The sodium cation helps pull off the chloride anion

B. The iodide anion activates the methoxide nucleophile

C. $S_N 2$ reaction of iodide ioc converts the alkyl chloride

to the more reactive alkyl iodide

D. The Nal changes the mechanism to $S_N 1$

Answer: C



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62. Assertion When 3- bromo propene , which contain a labelled $.^{13}\ C$ at C-1 position is refluxed with the methanol,

following products were obtained

$$H_2 \overset{13}{C} = CH - CH_2 Br \xrightarrow[CH_2OH]{ ext{boil}}$$

$$egin{aligned} H_2 \overset{13}{C} &= CH - CH_2Br \xrightarrow[CH_2OH]{ ext{boil}} \ H_2 \overset{13}{C} &= CH - CH_2OCH_3 + H_2C = CH - \overset{13}{C} & H_2OCH_3 \end{aligned}$$

Reason Methanol has an acidic proton bonded to oxygen.

- A. Both assertion and reason are connect and reason is the correct explanation of the assertion.
- B. Both assertion and reason are correct but reason is not the correct explantation of assertion.
- C. Assertion is correct but reason is incorrect
- D. Assertion is incorrect but reason is correct.

Answer: B



63. Match the quantity of column I with the quantity of column II:

	H			
	Reaction type		Halides	
	(a)	Most reactive in E2 reaction	(p)	—Br
	(b)	Equally reactive in E1	(q)	Br of the
	(c)	Produces same major product in E2	(r)	—Br
_	(d)	Loses chirality in both E1 and E2	(s)	—Br



64. 1,3-dichlorocyclopentane exist in three stereo isomeric forms, of which only two are chiral. If one mole of its achiral stereomer is treated with exactly one mole of its achiral

stereomer is treated with exactly with exactly one mole of NaOH in aquenous medium and , only mono substitution (S_N2) and mono-elimination(E2) occur producing chlorocyclopentanol and chlorocyclopentene, how many different products are expected ?



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65. In the following reaction, how many different $S_N 2$ products would be formed ?

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Chapter Test

- **1.** A chemist isolated a compound A with molecular formula $C_7H_{13}Br$. A undergoes very fast S_N1 reaction. Spectroscopic evidence indicated that compound A has the following structural characteristics.
- . It contains fnive sp_3 hybridised carbon atoms. Among those five SP^3 carbon atoms are three methyl groups, one CH_2 group and one CH group.
- . It also contains two SP_2 -hybridised carbon atoms . Also there is only one hydrogen atom attched to \mathfrak{sp}^2 carbons.
- . The compound contains a total of six allylic hydrogen atoms.

. The carbon atom that holds the Br has one H attached to it.

When compound A reacts with boiling water , it undergoes an S_N1 reaction and produces. two principal products B and C . Both B and C are alcohols with their molecular formula $C_7H_{14}O$. Among the two alcohols, B has the --OH group attached to an sP_3 carbon atom that has no H atoms bonded to it .

What can be said about the isomerism shown by the two alcohols B and C?

A. Both B and C show stereo isomerism and can be resolved into enantiomers

B. B and C are stereoisomers

C. Both B and C show stereoisomerism but only C Can be resolved into enantiomers

D. Neither B or C can be resolved into enantiomers

Answer: C



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- **2.** A chemist isolated a compound A with molecular formula $C_7H_{13}Br$. A undergoes very fast S_N1 reaction. Spectroscopic evidence indicated that compound A has the following structural characteristics.
- . It contains fnive sp_3 hybridised carbon atoms. Among those five SP^3 carbon atoms are three methyl groups, one CH_2 group and one CH group.

. It also contains two SP_2 -hybridised carbon atoms . Also there is only one hydrogen atom attched to sp^2 carbons.

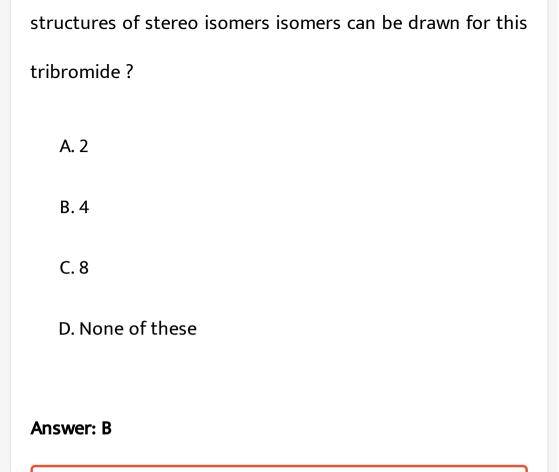
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presence of a Lewis acid catalys, a tribromide would result from addition of Br_2 to C=C . How many different

If the starting compound A is brominated in gas phase in





3. A chemist isolated a compound A with molecular formula $C_7H_{13}Br$. A undergoes very fast S_N1 reaction. Spectroscopic evidence indicated that compound A has the

following structural characteristics.

. It contains fnive sp_3 hybridised carbon atoms. Among those five SP^3 carbon atoms are three methyl groups, one CH_2 group and one CH group.

. It also contains two SP_2 -hybridised carbon atoms . Also there is only one hydrogen atom attched to ${\it sp}^2$ carbons.

- . The compound contains a total of six allylic hydrogen atoms.
- . The carbon atom that holds the Br has one H attached to it.

When compound A reacts with boiling water , it undergoes an S_N1 reaction and produces. two principal products B and C . Both B and C are alcohols with their molecular formula $C_7H_{14}O$. Among the two alcohols, B has the --OH group attached to an sP_3 carbon atom that has no H atoms bonded to it .

If the original compound A is treated with ${\rm LiAlH_4}$, a new compound $D(C_7H_{14})$ would be produced. How many different structure (s) can be drawn for this D ?

- A. One
- B. Two
- C. Three
- D. Four

Answer: A



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4. Assertion Consider the following two bromides I and II undergoing solvolysis reaction in boilding ethanol:

$$H_3C$$
 CH_3
 H_3C
 CH_3
 CH_3
 H_3C
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

I is less reactive than II in the given solvolysis reaction.

Reason The resonance stabilisation available with intermediate formed II is the important driving force.

- A. Both assertion and reason are connect and reason is the correct explanation of the assertion.
- B. Both assertion and reason are correct but reason is not the correct explantation of assertion.
- C. Assertion is correct but reason is incorrect

D. Assertion is incorrect but reason is correct.

Answer: A



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