

### About the Author



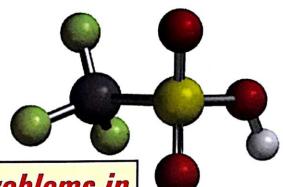
Mahendra Singh Chouhan (MSC Sir) is a renowned name in the realm of Organic Chemistry. Through a Chemical Engineer from Mumbai University, his great passion for the subject led him to impart guidance to IIT-JEE aspirants on a regular basis. His in depth knowledge and vast experience has helped innumerable students to achieve their dream of excelling at IIT, JEE and other such tough challenges.

He has launched a website to extend the benefits of his expertise beyond the geographical barriers to all those who dare to dream and seek-www.iitjeeorganic.com.

The website provides expert guidance in all the areas of the subject in a most skillful manner. There are quizzes, challenging questions, notes, e-books and videos etc. This website is a complete guide in itself for organic chemistry and has been designed for IIT-JEE aspirants, keeping in mind the various syllabi and CBSE.

Highly recommended for the high flyers.





# Advanced Problems in

# ORGANIC CHEMISTRY

for



M.S. Chouhan
Director

Vibrant Academy, Kota



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# A few words to the JEE Aspirants

Dear JEE aspirants,

I hope that this collection of problems will surely help you during your preparation for JEE. In this book, each chapter consists of two levels:

**Level 1 -** includes the problems having only one option correct. These problems are based on different facts and their twists.

Level 2 - includes unique approach which may be used to solve the problems altogether different from the prevailing trend followed by JEE. These approaches will undoubtedly help you in the quick revision of the key facts and their applications.

I wish all of you a grand success in the ensuing Joint Entrance Examination. Your valuable suggestions and constructive criticism for the betterment of the book are welcome.

M.S. Chouhan

# Preface

It is a matter of great pleasure for me to present the eleventh edition of "Advanced Problems in Organic Chemistry for JEE" before JEE aspirants. During my teaching experience, I felt that the facts may be made more and more clear to the students through problematic approach. Although an ocean of material in Organic Chemistry is available with the students, yet the approach to design the problems has been changed in recent years and if one tries to swim in this ocean, it will be a very difficult task. To make the students more familiar with trends and tricks how to solve problems, the present problem book has been presented. In the current scenario of stiff competition especially for JEE, one must be clear that almost all the sincere applicants are well equipped with the facts of subject, yet the winner is one who knows how to use these equipments with accuracy and efficiency. As an experienced teacher, I would like to suggest students three golden rules to score high in Organic Chemistry:

- 1. Don't get behind
- 2. Work out a number of problems of different types
- 3. Revise through short notes / learning chart.

I hope that the present book will cater to the needs of JEE aspirants & as a matter of fact, they will enjoy the present venture and I would feel rewarded if this book is found helpful to the students and teachers in real terms. All attempts have been made to make the book error free however a few misprints may inadvertently creep.

I acknowledge the blessing and support of my mother Smt. Raj Kanwar, father Shri B.S. Chouhan, brother Dr. V.S. Chouhan, my wife and daughter. They inspired me all the time during the preparation of this book.

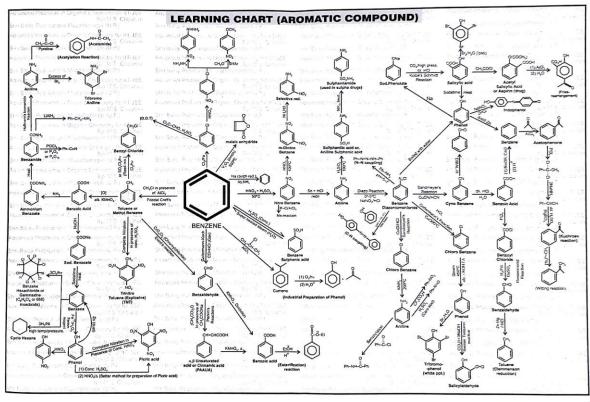
The support and valuable suggestions from my colleagues especially Mr. N. Avasthi , Mr. V. K. jaiswal, Mr. Nitin Jain, Mr. N.K. Sethia, Mr. Vikash Gupta, Mr. Pankaj Joshi, Dr. S. Kothari, Mr. Vineet Khatri, Mr. Ashish Mishra, Mr. Manish Arora, Mr. Govind Khandelwal, Mr. Rahul Pareek, Mr. Rahul Malav, Mr. Divyesh Tiwari, Mr. Omkar Kelapure, Mr. Kishore Kilani, Mr. Mayank Pareek, Mr. Gurpreet Singh, Mr. Yogesh Jain, Madam Anjana Kamal , Mr. Aneet Choudhary, Mr. Shaliwahan Singh Rathore, Mr. Akshay Chaudhary, Mr. Hanuman Sahay, Mrs. Neha Joshi, Mrs. Neetu Jha, Mr. Kamlesh Gupta and Mr. Kumud Ranjan are highly acknowledged. I also pay my sincere thanks to all the esteemed members of M/s Shri Balaji Publications in bringing out this book in such a nice form.

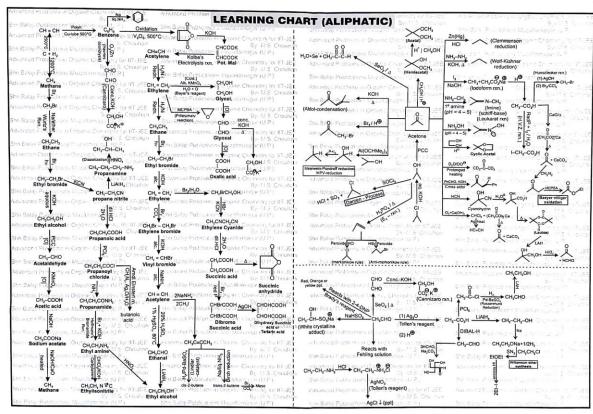
In the last, constructive criticism and valuable suggestions from the readers are most welcome to make the book more useful.

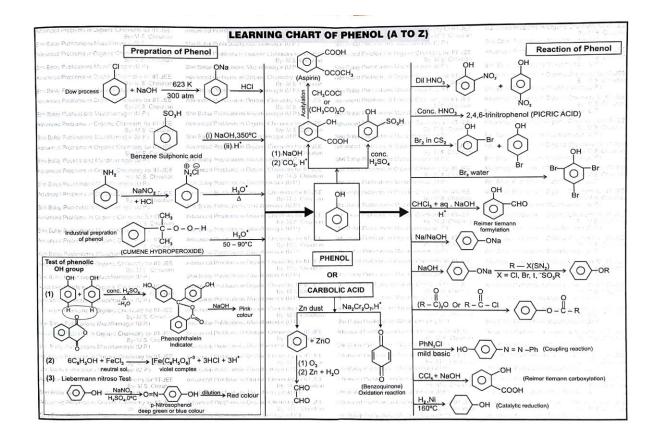
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# Contents

	1	General Organic Chemistry	1-72
	2	Isomerism (Structural & Stereoisomerism)	73-151
	3	Grignard Reagent	152-173
	4A	Hydrocarbons (Alkanes)	174-189
1	4B	Hydrocarbons (Alkenes)	190-253
3	4C	Hydrocarbons (Alkynes)	254-260
	5A	Alkyl Halides (Substitution Reaction)	261-297
	5B	Alkyl Halides (Elimination Reaction)	298-328
	5C	Alkyl Halides	329-341
1	6	Alcohol, Ether and Epoxides	342-388
	7	Aldehydes and Ketones	389-440
1	8	Aldol and Cannizaro Reaction	441-460
	9	Carboxylic Acid and their Derivatives	461-479
Boulding .	10	Amines	480-486
	1.1	Carbene and Nitrene	487-506
	12	Aromatic Compounds	507-578
	13	Practical Organic Chemistry	579-584
	14	Biomolecules	585-596
	15	IUPAC Names	597-624
	•	Learning Chart	









Reagents

A. HCl	B. Br <sub>2</sub>	C. Hg(OAc) <sub>2</sub> in H <sub>2</sub> O	$D.B_2H_6(BH_3)$ in ether
E. H <sub>2</sub> O <sub>2</sub>	F. KMnO <sub>4</sub> in H <sub>2</sub> O	G. HOBr	H. NaBH <sub>4</sub>

In each reagent box write a letter designating the best reagent and condition selected from the above list of reagents.

Reactant	Reagent		Product	
	(i)		(CH <sub>3</sub> ) <sub>2</sub> CHCH(Cl)CH <sub>3</sub> 2-Chloro-3-methyl butane	
	(ii)		(CH <sub>3</sub> ) <sub>2</sub> CHCHBrCH <sub>2</sub> Br 1,2-dibromo-3-methyl butane	
$(CH_3)_2CHCH = CH_2$ 3-methyl 1-butene	(iii)		(CH <sub>3</sub> ) <sub>2</sub> CHCHOHCH <sub>2</sub> Br 1,bromo-3-methyl 2-butanol	
	(iv)		(CH <sub>3</sub> ) <sub>2</sub> CHCH(OH)CH <sub>3</sub> 3-methyl-2-butanol	
	(v)		(CH <sub>3</sub> ) <sub>2</sub> CHCH(OH)CH <sub>2</sub> OH 3-methyl-1,2-butanediol	

2. Propene  $(CH_3 - CH = CH_2)$  can be transformed to compounds (a to j) listed in the left-hand column.

Write letter designating the reagent, you believe will achieve desired transformation. In the case of a multi step sequence write the reagent in the order they are to be used.

	Desired Product	No. of Steps	Write options		Reagent List
a.	CH <sub>3</sub> CHBrCH <sub>2</sub> Br	one	1	A.	Hg(OAc) <sub>2</sub> in H <sub>2</sub> O
ъ.	(CH <sub>3</sub> ) <sub>2</sub> CHOH	two		В.	B <sub>2</sub> H <sub>6</sub> in THF

ci	CH₃CH₂CH₂OH	two	C.	NaBH <sub>4</sub> in alcohol
d.	CH₃COCH₃	three	D.	Br <sub>2</sub> in CH <sub>2</sub> Cl <sub>2</sub>
e.	CH <sub>3</sub> CH <sub>2</sub> CHO	three	E.	H <sub>2</sub> O <sub>2</sub> in aqueous base
f.	CH <sub>3</sub> CH(OH)CH <sub>2</sub> Br	one	F.	HOBr (NBS in aqueous acetone)
g.	(CH <sub>3</sub> ) <sub>2</sub> CHBr	one	G.	${ m HBr~in~CH}_2{ m Cl}_2$
h, k.	CH <sub>3</sub> CH(OH) CH <sub>2</sub> OH	two	н.	OsO <sub>4</sub> in ether
i.	$CH_3 - CH_2 - CH_2 - Cl$	three	I.	Thionyl chloride (SOCl <sub>2</sub> )
j.	$CH_3 - C \equiv CH$	two	J.	NaHSO <sub>3</sub> in aqueous acetone
			ĸ.	NaOH in alcohol and reflux
			L.	NaNH <sub>2</sub> (strong base)

**3.** In each reaction box write a single letter designating the best reagent and condition selected from the list at bottom of the page.

(F.S.,  $\rightarrow$  first step, S.S  $\rightarrow$  second step, T.S.  $\rightarrow$  third step)

Reaction	Reactant	Options	Product
1.	CH <sub>3</sub>		OH CH <sub>3</sub> OCH <sub>3</sub>
2.	CH <sub>3</sub>	F.S	CH <sub>3</sub>
3.	CH <sub>3</sub>	F.S. □ → S.S. □	ОН
4.	°	FS. □ S.S. □	Ph
5.		F.S	Ph

A. NaBH <sub>4</sub> /alcohol	B. Ph -CO <sub>3</sub> H/CH <sub>2</sub> Cl <sub>2</sub>	C. PCC	<b>D.</b> CH <sub>3</sub> ONa/CH <sub>3</sub> OH
E. B <sub>2</sub> H <sub>6</sub> in THF	<b>F.</b> H <sub>2</sub> O <sub>2</sub> /aq. NaOH	<b>G.</b> H <sub>3</sub> PO <sub>4</sub> & heat	H. AlCl <sub>3</sub> /C <sub>6</sub> H <sub>6</sub>
I. O <sub>3</sub> in CH <sub>2</sub> Cl <sub>2</sub>	J. Br <sub>2</sub> in CH <sub>2</sub> Cl <sub>2</sub>	<b>K.</b> 20% KOH & heat	L. Ph – Li/ether

**4.** Match the reagents a-j with products A-J. There is one best product for each reaction.

The molecule (x) is the starting material for all reactions in problem. Do the ones you know first and then tackle the rest by deductive reasoning

first and then tackle the rest by deductive reasoning					
Products		Reagents	Option		
Br Br		H <sub>2</sub> O heat, pH 7	3		
A B B	(b)	F <sub>3</sub> C O OH			
ОН	(c)	tBuOK, polar aprotic solvent			
Br On	(d)	(1) O <sub>3</sub> , ether (2) H <sub>2</sub> O, NaOH, H <sub>2</sub> O <sub>2</sub>			
D E	(e)	Br <sub>2</sub> ,CCl <sub>4</sub>	3		
Br Br Br	(f)	NBS, hv, CCl <sub>4</sub>			
F G Br	(g)	(1) H <sub>3</sub> O(+) (2) NaOH, H <sub>2</sub> O			
OH Br Br	(h)	(1) BH <sub>3</sub> , ether (2) H <sub>2</sub> O <sub>2</sub>			
Br Br Br Br	(i)	(1) OsO <sub>4</sub> (2) NaOH, H <sub>2</sub> O			
J	(I)	H <sub>2</sub> /Pd/C(EtOH)			

#### 5. Match the column:

	Column (I)		Column (II)
(a)	$CH_3$ — $C \equiv C$ — $CH_3$	(p)	cis-product with H <sub>2</sub> /Pd - BaSO <sub>4</sub>
(b)	CH <sub>3</sub> —CH <sub>2</sub> —C≡CH	(q)	Trans-product with Na/liq. NH <sub>3</sub>
(c)	CH <sub>3</sub> —C ≡CH	(r)	White with amm. AgNO <sub>3</sub>
(d)	$CH_3$ — $C \equiv C$ — $Et$	(s)	H <sub>2</sub> gas with Na

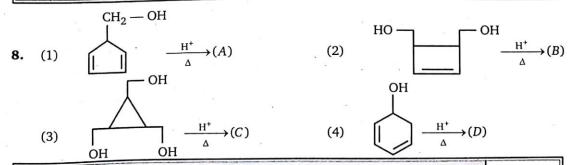
### 246 ORGANIC Chemistry for IIT-JEE

### 6. Match the column I with column II and with column III (Matrix).

Column-I			Column- II	(	Column- III
Reaction		Reaction Nature of product formed		present (Conside	er only one isomer of racemic mixture or
(a)	$ \begin{array}{c c}  & & \\$	(p)	Racemic mixture	(w)	0
(b)	$ \begin{array}{c}                                     $	(q)	Meso	(x)	1
(c)	$ \begin{array}{c}  & \xrightarrow{Br_2} \\  & \text{CCl}_4 \end{array} $	(r)	Diastereomer	(y)	2
(d)	$CH_3$ $C = C$ $CH_3$ $CCL_4$ $CCL_4$	(s)	Vicinal dihalide	(z)	. 3

#### 7. Match the column I and II.

	Column (I)		Column (II)
	Reaction		Product
(a)	$\underbrace{\frac{(1) \text{OsO}_4}{(2) \text{NaOH}, \text{H}_2\text{O}}}$	<b>(</b> p)	OH
(b)	(1) BH <sub>3</sub> /ether (2) H <sub>2</sub> O <sub>2</sub> , NaOH, H <sub>2</sub> O	<b>(q)</b>	OH
(c)	Cl <sub>2</sub> , H <sub>2</sub> O →	<b>(r)</b>	ОН
(d)		(s)	Cl



Sum of molecular mass of A, B, C, D (i.e. A+B+C+D) is equal to:

- 9. (1)  $C_2FClBrI \xrightarrow{H_2} (A)$  (exclude stereoisomer)
  - (2)  $C_4H_8$  (alkene)  $\xrightarrow{H_2}$  (B) (exclude stereoisomer) (all isomers)

### Total number of products A and B (i.e. A + B) is equal to:

10.

U.	
Reaction 1	Reaction 2
$\begin{array}{c c} CH_{3} \\ H & Br \\ \hline CH \\ \parallel (cis) \xrightarrow{Br_{2}} (P) \\ CH \\ H & Br \\ \hline CH_{3} \end{array}$	$\begin{array}{c c} CH_{3} \\ H & Br \\ \hline CH \\ \parallel (trans) & Br_{2} \\ CH \\ CH \\ \hline Br \\ CH_{3} \\ \end{array}$
Reaction 3	Reaction 4
$\begin{array}{c c} CH_3 \\ H & Br \\ \hline \\ CH \\ \parallel (cis) & Br_2 \\ CCl_4 \\ \downarrow \\ CH_3 \\ \end{array} (R)$	$\begin{array}{c c} CH_3 \\ H & Br \\ \hline CH \\ \parallel (trans) & \xrightarrow{Bt_2} (S) \\ CH \\ \downarrow \\ CH_3 \end{array}$

Sum of products P, Q, R, S (i.e. P + Q + R + S) is equal to :

#### 11. Comprehension

Vladimir Markovnikov rule:

Alkenes undergo electrophilic addition reactions. It is triggered by the acid acting as a electrophile toward  $\pi$ -electrons of the double bond.

Markovnikov's rule states that when an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen atom adds to the carbon that has the greater number of hydrogen, e.g.,

$$CH_3 + H - Cl$$
  $\xrightarrow{0^{\circ}C}$   $Cl$ 

1-methyl cyclopentene

1-chloro-1-methyl cyclopentane

(fast)

Mechanism:

Step - 1 
$$CH_3 + H - Cl$$
  $\longrightarrow$   $CH_3 + CH_3$   $Cl^{\Theta}$ 

Step - 2  $CH_3 + CH_3 + CH_3$   $Cl^{\Theta}$ 

Which of the following is most reactive toward Markovnikov addition?

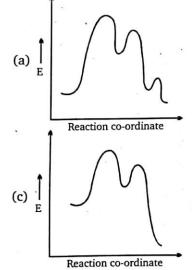


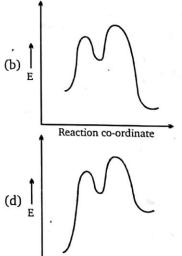






B. What is the energy profile for the given reaction?





C. In which of following reactions carbocation rearrangement is possible?

(a)  $(CH_3)_2CH - CH = CH_2 \xrightarrow{HCl}$ (b)  $(CH_3)_3C - CH = CH$ 

(a) 
$$(CH_3)_2CH - CH = CH_2 - \frac{HCI}{0^{\circ}C}$$

(b) 
$$(CH_3)_3C - CH = CH_2 \frac{HBr}{0°C/Cl_4}$$

Reaction co-ordinate

(c) 
$$Ph - CH_2 - CH = CH_2 - \frac{HBr}{CCl_4}$$

(d) All of these

Identify the major products 
$$r_1$$
,  $r_2$  and  $r_3$  in the given reactions.

$$CH_3 \xrightarrow{HBr} r_1$$

$$HBr \xrightarrow{CH_3OH} r_2$$

$$HBr \xrightarrow{D_2O} r_3$$

$$CH_3 \xrightarrow{CH_3} CH_3$$

$$CH_3 \xrightarrow{CH_3}$$

- E. In which of the following reactions, product is racemic mixture?
  - (a)  $CH_3 CH_2 CH = CH_2 \xrightarrow{HBr} CCl_4$

(b) 
$$_{\text{CH}_3}^{\text{H}}$$
  $_{\text{C}}$   $_{\text{C}}$   $_{\text{C}}$   $_{\text{C}}$   $_{\text{HBr}}$   $_{\text{CCI}_4}$ 

(c) 
$$\underset{\text{(cis)}}{\text{CH}_3} = \underset{\text{(cis)}}{\text{CCH}_3} \xrightarrow{\text{HBr}}$$

- (d) All of these
- F. In which of the following reactions, diastereomers will be formed?

(a) 
$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CCI_4$ 
(b)  $CI_4$ 
 $CCI_4$ 
 $CCI_4$ 
(c)  $CI_4$ 
 $CI_4$ 

#### 12. Comprehension

$$\label{eq:ch3} \begin{split} \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH} &== \operatorname{CH}_2 + \operatorname{CH}_3 \operatorname{OH} \xrightarrow{\operatorname{H}^\oplus} \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH} - \operatorname{CH}_3 \\ & | \\ \operatorname{OCH}_3 \end{split}$$

Consider the above reaction and answer A to E.

A. What is electrophile in first step?

(c) 
$$CH_3 - CH_2 - \overset{\oplus}{C}H - CH_3$$

- B. What is nucleophile in first step?
  - (a) CH<sub>3</sub>OH
  - (c)  $H_2O$
- C. What is electrophile in second step?

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

**D.** What is nucleophile in second step?

(a) 
$$CH_3 - CH_2 - CH = CH_2$$

- (c)  $H_2O$
- E. Which step is rate determining step?
  - (a) attack of nucleophile CH<sub>3</sub>OH
  - (c) attack of nucleophile H2O

- (b). H<sup>⊕</sup>
- (d) HO<sup>⊕</sup>
- (b) 1-butene
- (d)  $CH_3 O CH_3$
- (b) H<sup>⊕</sup>

(d) 
$$\operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH}_2$$

- (b) CH<sub>3</sub>OH
- (d)  $CH_3 O CH_3$
- (b) attack of electrophile H<sup>⊕</sup>
- (d) attack of electrophile CH<sub>3</sub>

#### 13. Match the column I and II:

	Column (I)	Column (II)  Reagent						
	Conversion							
(a)	$ \begin{array}{c}  & \xrightarrow{\text{CH}_3} & \xrightarrow{\text{Br}} \\  & \xrightarrow{\text{Br}} & \xrightarrow{\text{Br}} \end{array} $	<b>(p)</b>	$SO_2Cl_2/hv$ (2 equivalent)					
(b)	$\overset{CH_3}{\longrightarrow}\overset{CH_2-Cl}{\longrightarrow}$	( <b>q</b> )	NBS (2 equivalent)					
(c)	CH <sub>3</sub> Br Ccl	<b>(r)</b>	NBS then $\mathrm{SO_2Cl_2}/hv$					
(d)	$\overset{\text{CH}_3}{\longrightarrow} \overset{\text{CH}_2\text{-Cl}}{\longrightarrow}$	(s)	SO <sub>2</sub> Cl <sub>2</sub> / hv then NBS					

#### **ANSWERS — LEVEL 2**

1. (i) 
$$-A$$
; (ii)  $-B$ ; (iii)  $-G$ ; (iv)  $-C$ ; (v)  $-F$ 

**2.** 
$$a - D$$
;  $b - A$ ,  $C$ ;  $c - B$ ,  $E$ ;  $d - A$ ,  $C$ ,  $F$ ;  $e - B$ ,  $E$ ,  $F$ ;  $f - F$ ;  $g - G$ ;  $h - I$ ,  $K$ ;  $i - B$ ,  $E$ ,  $I$ ;  $j - D$ ,  $L$ 

**4.** 
$$a - C$$
;  $b - D$ ;  $c - A$ ;  $d - F$ ;  $e - I$ ;  $f - J$ ;  $g - E$ ;  $h - H$ ;  $i - B$ ;  $j - G$ 

**5.** 
$$a-p, q; b-r, s; c-r, s; d-p, q$$

**6.** 
$$a-r$$
,  $s-z$ ;  $b-p$ ,  $s-y$ ;  $c-p$ ,  $s-y$ ;  $d-q$ ,  $s-y$ 

7. 
$$a-r$$
;  $b-p$ ;  $c-q$ ;  $d-s$ 

8. 
$$A + B + C + D = 312$$
  
10.  $P + Q + R + S = 8$ 

9. 
$$A+B=5$$
  
11.  $A-b$ ;  $B-c$ ;  $C-d$ ;  $D-b$ ;  $E-d$ ;  $F-d$ 

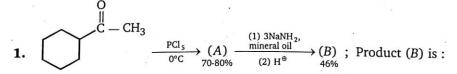
**12.** 
$$A - b$$
;  $B - b$ ;  $C - c$ ;  $D - b$ ;  $E - b$ 

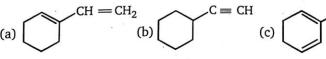
# 4c

# **HYDROCARBONS (ALKYNES)**



# LEVEL- 1





2. 
$$\frac{Br_2}{CCl_4} \xrightarrow{\text{(i) alc.KOH}} (A); \text{ Product (A) is :}$$

(a) 
$$H_2C = CH - CH = CH_2$$

(b) 
$$CH_3 - C \equiv C - CH_3$$

(c) 
$$CH_3 - CH_2 - C \equiv CH$$

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

3. 
$$CH_3CH_2C \equiv CH \xrightarrow{NaNH_2} I \xrightarrow{Et_2O} J \xrightarrow{H^{\oplus}} (K)$$

Product (K) of the above reaction is:

$$(a) \qquad C = C - Et$$

$$(b) \bigcap_{C = C - Et}$$

$$\begin{array}{c} \text{OH} \\ \text{(c)} \end{array} = \text{C} - \text{CH}_2 - \text{CH}_3 \\ \end{array} \tag{C}$$

4. 
$$CH_3 - CH_2 - CH_2 - C \equiv CH + LiNH_2 \longrightarrow (A) \xrightarrow{(CH_3)_2 SO_4} (B)$$
Lithium

Give the structural formula of compound (B):

(a) 
$$CH_3 - (CH_2)_2 - C \equiv C - SO_3H$$

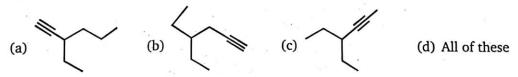
(b) 
$$CH_3 - (CH_2)_2 - C \equiv C - CH_3$$

(c) 
$$CH_3 - (CH_2)_2 - C \equiv C - CH_2 - O - S - H$$

(d) 
$$\mathrm{CH_3} - \mathrm{CH_2} - \mathrm{C} \equiv \mathrm{C} - \mathrm{CH_2}$$

; This conversion can be acheived by :

- (a) NaNH<sub>2</sub>, CH<sub>3</sub>CHO
- (c) KOH, CH<sub>3</sub> CH<sub>2</sub> Br
- (b) NaNH<sub>2</sub>, CH<sub>3</sub>—CH<sub>2</sub>—CH<sub>2</sub>—Br
- (d) KOH, CH<sub>2</sub>—CH<sub>2</sub>
  | | |
  Br Br
- 6. Which alkyne will give 3-ethylhexane on catalytic hydrogenation?



Reactant P gives products Q or R.

$$(CH_2)_4$$
  $\rightarrow$   $(CH_2)_4$   $\rightarrow$   $(CH_2)_4$   $\rightarrow$   $(H_2C)_4$   $\rightarrow$   $(H_2$ 

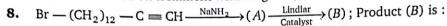
The possible reagents are:

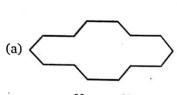
- (I) 2Na/liq. NH<sub>3</sub>
- (II) H<sub>2</sub>/Pd/CaCO<sub>3</sub>(quinoline)
- (III) 2H2/Pd/C

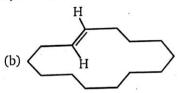
The correct statement with respect to the above conversion is/are:

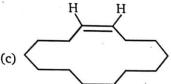
- (a) Q is obtained on treatment with reagent (I)
- (b) R and Q are obtained on treatment with reagent (II)
- (c) R is obtained on treatment with reagent (I)

(d) R is obtained on treatment with reagent (II)









(d) Br — 
$$(CH_2)$$
 —  $CH$  =  $CH_2$ 

Ph — C  $\Longrightarrow$  CH  $\xrightarrow{\text{MeO}^-}$  Major product of the reaction is :

(a) 
$${Ph \atop H} C = C < H$$

(b) 
$$\begin{array}{c} Ph \\ H \end{array}$$
  $C = C \begin{array}{c} OMe \\ H \end{array}$  (d)  $Ph - C = CH_2$   $OMe$ 

(c) 
$$Ph - C \equiv C - OMe$$

(d) Ph - 
$$G = CH_2$$

10. Ph—C—CH<sub>3</sub> 
$$\xrightarrow{3\text{NaNH}_2}$$
 (A); Product (A) is

(a) 
$$Ph$$
— $CH$ = $CH_2$ 

(b) 
$$Ph$$
— $C \equiv CH$ 

(a) 
$$Ph$$
— $CH$  =  $CH_2$  (b)  $Ph$ — $C$  =  $CH_3$  (c)  $Ph$ — $CH_3$  (d)  $Ph$ — $C$  =  $CNa$ 

Which combination is best for preparation of the compound (A) shown below? 11.

$$H \longrightarrow C - CH_2CH_2CH_2C = CH_3CH_2 (A)$$

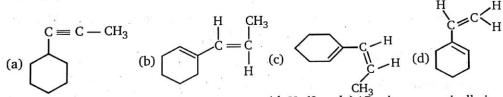
Which one of the following is the intermediate in the preparation of a ketone by hydration of 12. an alkyne in the presence of sulfuric acid and mercury (II) sulphate?

To carry out above conversion, (A) and (B) respectively, are:

- (a)  $NaNH_2$ ,  $Cl CH_2 CH_2 CH_2 Br$
- (b) NaNH<sub>2</sub>,  $F CH_2 CH_2 CH_2 Br$
- (c) NaNH<sub>2</sub>,  $I CH_2 CH_2 CH_2 Br$ (d) NaNH<sub>2</sub>,  $I CH_2 CH_2 CH_2 I$

14. 
$$H - C \equiv C - Ph$$
  $\xrightarrow{I_2}$  Product; Product obtained in this reaction is:

**15.** 
$$C \equiv CH \xrightarrow{\text{(i) NaNH}_2, NH}_3 (A) \xrightarrow{\text{H}_2}_{\text{Lindlar catalyst}} (B)$$
; Product (B) is:



- Which of the following alkyne on treatment with  $H_2(2 \text{ mole})$ / Pt gives an optically inactive 16. compound?
  - (a) 3-Methyl-1-pentyne

(b) 4-Methyl-1-hexyne

(c) 3-Methyl-1-heptyne

- (d) None of the above
- Red hot Cu tube  $\rightarrow$  (B), Product (B) of the reaction is: CaC<sub>2</sub> 17.
  - (Calcium carbide) (a) Toluene
- (b) Ethyl-benzene
- (c) Benzene
- (d) Butyne
- What is the final product, C, of the following reaction sequence? 18.

Compound (X) will be:

(a) 
$$CH = CH - C \equiv CH$$

(b) 
$$CH - CH_2 - C \equiv CH$$

(c) 
$$CH - CH_2 - C \equiv CH$$

(d) 
$$C = CH - C \equiv CH$$

- 20. Choose the sequence of steps that describes the best synthesis of 1-butene from ethanol:
  - (a) (1) NaC  $\equiv$  CH; (2) H<sub>2</sub>, Lindlar Pd
  - (b) (1) NaC  $\equiv$  CH ; (2) Na, NH<sub>3</sub>
  - (c) (1) HBr, heat; (2) NaC  $\equiv$  CH; (3) H<sub>2</sub>, Lindlar Pd
  - (d) (1) HBr, heat; (2) KOC(CH<sub>3</sub>)<sub>3</sub>, DMSO; (3) NaC  $\equiv$  CH; (4) H<sub>2</sub>, Lindlar catalyst
- Which alkyne yields butanoic acid (CH3CH2CO2H) as the only organic product on 21. treatment with ozone followed by the hydrolysis?
  - (a) 1-Butyne
- (b) 4-Octyne
- (c) 1-Pentyne
- (d) 2-Hexyne

**22.** (A) 
$$\xrightarrow{2H_2}$$
  $\xrightarrow{Pt}$   $CH_2 - CH_2 - CH_2$ 

Carlina oxide

Unit of unsaturation in compound (A)?

- (a) 7
- (b) 8
- (c) 9
- (d) 10

Product (C) of above reaction is:

(a)  $H_2C = CH_2$ 

(b)  $CH_3 - C \equiv C - CH_3$ 

(c)  $HC \equiv CH$ 

- (d)  $CH_3 CH = CH CH_3$
- To convert 1-butyne to 1-D-butanal, one would carry out the following steps: 24.
  - (I) Sodium amide, then D2O
  - (II) Disiamy lborane, then hydrogen peroxide/sodium hydroxide
  - (III) The transformation can not be carried out with the indicated reagents.

  - (a) I, followed by II (b) II, followed by I (c) III
- (d) II

- An unknown compound (A) has a molecular formula  $C_4H_6$ . When (A) is treated with excess of Br2 a new substance (B) with formula C4H6Br4 is formed. (A) forms a white ppt. with ammonical silver nitrate solution. (A) may be:
  - (a) But-1-yne

(b) But-2-yne

(c) But-1-ene

- (d) But-2-ene
- 26. One mole of 1,2-dibromopropane on treatment with X moles of NaNH2 followed by treatment with ethyl bromide gave a pentyne. The value of X is:
- (b) Two
- (c) Three
- (d) Four

$$CH_3 \atop | CH_3 - CH - C \equiv CH \qquad excess HBr$$

The product of the above reaction is:

$$\begin{array}{c|cccc} & CH_3 & Br & Br \\ & & & & \\ & & & & \\ \end{array}$$
 (a) 
$$CH_3 - CH - CH - CH_2$$

$$CH_3$$
 Br  
| | |  
(c)  $CH_3 - CH - C - CH_3$   
| Br

**28.** 
$$CH_3 - C \equiv C - CH_3 \xrightarrow{\text{Cold KMnO}_4} (A)$$

Product (A) is:

(d) 
$$O = CH - CH_2 - CH_2CH = O$$

In which reaction last product is  $Ph - C \equiv CH$ ? 29.

(a) 
$$C_6H_5 \stackrel{\text{Br}}{\underset{|}{\leftarrow}} C - CH_3 \xrightarrow{3\text{NaNH}_2} \xrightarrow{\text{NH}_4Cl} \xrightarrow{\text{NH}_4Cl}$$

(b) 
$$C_6H_5CH = CH_2 \xrightarrow{Br_2} \xrightarrow{3NaNH_2} \xrightarrow{NH_4Cl}$$

(c) 
$$C_6H_5 - C - CH_3 \xrightarrow{PCl_5} \xrightarrow{3NaNH_2} \xrightarrow{NH_4Cl} \xrightarrow{NH_4Cl}$$

(d) All

(d)

**30.** Predict the product of the following reaction sequence.

ethyne 
$$\frac{\text{(1) excess NaNH}_2}{\text{(2) excess I}-\text{CH}_2-\text{(CH}_2)_2-\text{CH}_3}$$
  
 $\text{(3) H}^{\oplus}$ 

(a) 6-iodo-1-hexyne

(b) 1-hexyne

(c) 5-decyne

(d) 1-iodo-1-hexene

31. The best sequence of reactions to prepare 2-heptanone is

(a) propyne 
$$\xrightarrow{\text{NaNH}_2} X \xrightarrow{n-C_4 \text{H}_9 \text{Br}} Y \xrightarrow{\text{H}_2 \text{O}, \text{Hg}^{2+}} H_2 \text{SO}_4$$

(b) ethyne 
$$\xrightarrow{\text{NaNH}_2} X \xrightarrow{n-C_5H_{12}\text{Br}} Y \xrightarrow{\text{H}_2\text{O},\text{Hg}^{2^+}} H_2\text{SO}_4$$

(c) 
$$1 - \text{hexyne} \xrightarrow{\text{NaNH}_2} X \xrightarrow{\text{CH}_2\text{Br}} Y \xrightarrow{\text{H}_2\text{O.Hg}^{2+}} H_2\text{SO}_4$$

(d) 1-pentyne 
$$\xrightarrow{\text{NaNH}_2} X \xrightarrow{\text{C}_2\text{H}_5\text{Br}} Y \xrightarrow{\text{H}_2\text{O},\text{Hg}^{2+}} H_2\text{SO}_4$$

32. The major product of the reaction of 2-butene with cold alkaline KMnO<sub>4</sub>, is

(a) (b) 
$$\bigcirc$$
 (c)  $\bigcirc$ 

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

# **ALKYL HALIDES**

Substitution Reactions  $(S_{N^1}, S_{N^2}, S_{N^i})$ 



# LEVEL- ]

1. Which of the following is not expected to be intermediate of the following reaction?

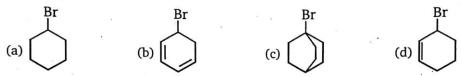
$$\stackrel{\text{I}}{\longrightarrow} \stackrel{\text{H}_2\text{O}}{\longrightarrow} \stackrel{\text{OH}}{\longrightarrow}$$

(b) t



2. Br 
$$\xrightarrow{\text{CH}_3}$$
 H  $\xrightarrow{\text{NaI}}$  + NaI  $\xrightarrow{\text{Acetone}}$  product; S<sub>N<sup>2</sup></sub> product of the reaction is :
$$CH_2 - CH_3$$

**3.** Rate of  $S_{N^2}$  will be negligible in :



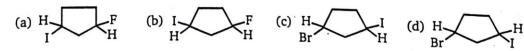
**4.** What is the major product obtained in the following reaction? CH<sub>2</sub>-Br

$$(a) \qquad (b) \qquad (c) \qquad (d) \qquad (d)$$

5.  $Cl - CH_2 - CH_2 - CH_2 - Cl + I^- \xrightarrow{DMF}$  product; Major product of this reaction is:  $CH_3$ 

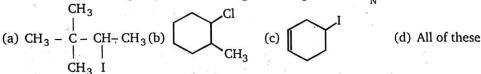
- **6.** Which of the following expressions is representative of the rate law for a  $S_{N^2}$  reaction?
  - (a) Rate = k [electrophile]
- (b) Rate = k [electrophile] [nucleophile]
- (c) Rate = k [nucleophile]<sup>2</sup>
- (d) Rate =  $k[electrophile]^2$

7.  $H \xrightarrow{F+} NaI (1 \text{ mole}) \xrightarrow{Acetone} (A)$ ; Major product of this reaction is:

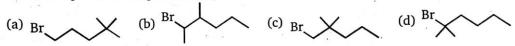


#### **ALKYL HALIDES (SUBSTITUTION)**

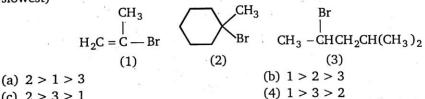
**8.** Which of the following alkyl halide undergo rearrangement in  $S_{N^1}$  reaction?



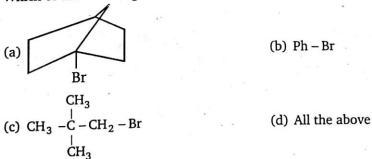
- 9. Arrange the following three chlorides in decreasing order towards S<sub>N1</sub> reactivity.
  - (1) Cl (2) Cl (3) Cl (b) 2 > 3 > 1 (c) 2 > 1 > 3 (d) 3 > 2 > 1
- 10. Which compound undergoes nucleophilic substitution with NaCN at the fastest rate?

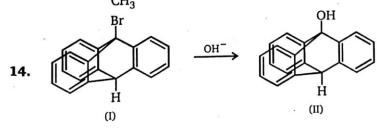


11. Rank the following in order of decreasing rate of solvolysis with aqueous ethanol (fastest  $\rightarrow$  slowest)



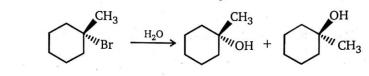
- (c) 2 > 3 > 1
   (4) 1 > 3 > 2
   The reaction of 4-bromobenzyl chloride with sodium cyanide in ethanol leads to the formation of:
  - (a) 4-bromobenzyl cyanide
- (b) 4-cyanobenzyl chloride
- (c) 4-cyanobenzyl cyanide
- (d) 4-bromo-2-cyanobenzyl chloride
- 13. Which of the following reactant will not favour nucleophilic substitution reaction?

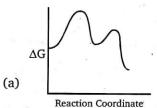


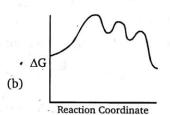


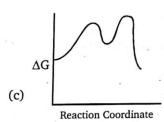
Conversion of I to II:

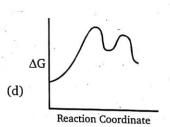
- (b) takes place by S<sub>N²</sub>(d) does not take place
- (a) takes place by  $S_{N^1}$ (c) takes place both by  $S_{N^1}$  and  $S_{N^2}$
- 15. Which is the correct reaction coordinate diagram for the following solvolysis reaction?



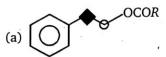


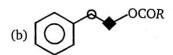






product; Product of this reaction is:





(c) both (a) and (b)

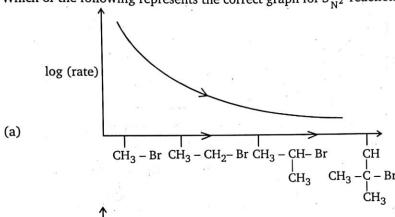
(d) None of these

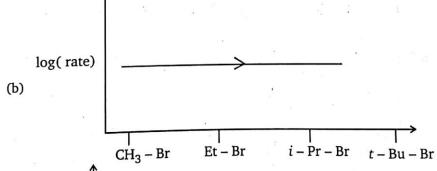
17. 
$$CH_3$$
 $\longrightarrow$   $(A)$   $\xrightarrow{CH_3SNa}$   $(B)$ , Product  $(B)$  is:

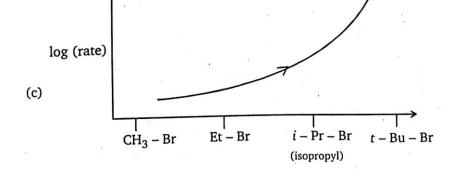
(a) 
$$CH_2$$
-S- $CH_3$ 

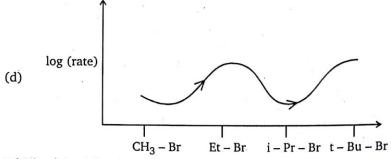
(d) None of these

18. Which of the following represents the correct graph for  $S_{N^2}$  reaction?

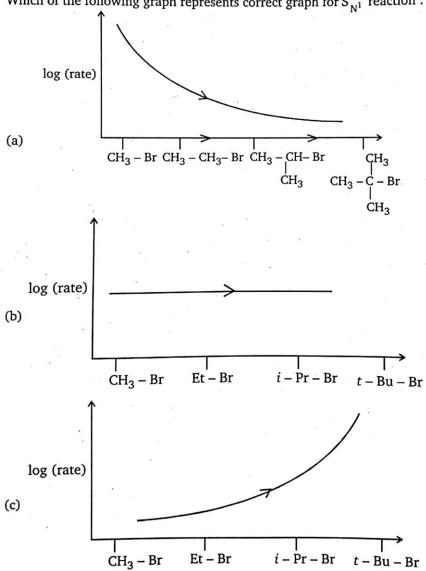


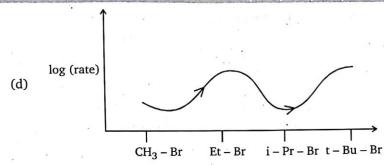




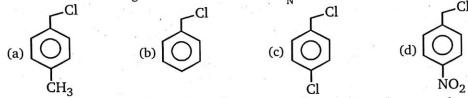


**19.** Which of the following graph represents correct graph for  $S_{N^1}$  reaction :





**20.** Which of the following is most reactive toward  $S_{N^2}$  reaction?



21. Among the given pairs, in which pair first compound reacts faster than second compound in  $S_{N^1}$  reaction?

(a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - Br \text{ or } CH_3 - CH_2 - CH - CH_3$$

$$CH_3 \qquad CH_3$$
(b)  $CH_3 - C - CH_2 - CH_2 \text{ or } CH_3 - CH - CH - CH_3$ 

$$Br \qquad Br$$

$$CH_3$$
  $CH_3$   $CH_3$ 

22. What is the major product of the following reaction?

$$H_2C = CH - CH_2 - OH \xrightarrow{HBr} Product$$

(b) 
$$H_2C = CH - CH_2 - Br$$
  
OH

(d) 
$$CH_3 - CH - CH_2 - OH$$

**23.**  $S_{N^1}$  and  $S_{N^2}$  products are same with (excluding stereoisomer):

**24.** Consider the nucleophilic attacks given below. Select in each pair that shows the greater  $S_{N^2}$  reaction rate.

or

or

$$A$$
)  $Br + CN$  or

(B) 
$$H_3C - Br + -SH$$

 $H_3C - Br + CH_3SH$ 

$$(C)$$
  $\longrightarrow$   $Br + Cl^-$  or

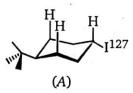
$$\begin{array}{c}
 & \text{Br} + I^{-} \text{ in DMSO} \\
\end{array}$$

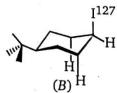
(D) 
$$\bigcirc$$
 Br + Cl

(b) (II); (III); (V); (VIII)

(d) (I); (III); (V); (VII)

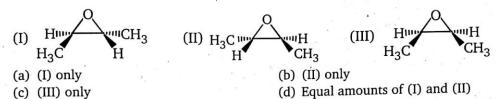
**25.** Which of the two stereoisomers of 4*t*-butylcyclohexyl iodide ( $^{127}$  I<sup>-</sup>) will undergo S<sub>N<sup>2</sup></sub> substitution with  $^{128}$  I<sup>-</sup> faster, and why?





- (a) A will react faster because it is the more stable of the two isomers
- (b) A will react faster because it will yield a more stable product, and the transition state for both reactions is of the same energy
- (c) A will react faster because the approach of <sup>128</sup> I<sup>-</sup> can depart unhindered.
- (d) B will react faster because it is less stable than A, and the transition state for both reactions is of the same energy

**26.** (*Z*)-2-Butene reacts with  $Br_2/H_2O$ . The resulting bromohydrin when treated with methoxide in methanol undergoes an intramolecular  $S_{N^2}$  reaction. Taking into consideration the stereochemical consequences of the reaction mechanism involved, choose the final product(s) of these transformations.



27. Rank the following species in order of decreasing nucleophilicity in a polar protic solvent (most → least nucleophilic):

28. Identify products of the given reactions:

Reaction-1

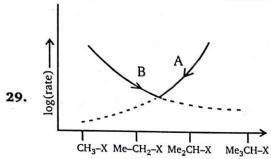
NMe<sub>2</sub>

$$CH_3CO_2Na \atop CH_3CO_2Na \atop CH_3CO_2Na \atop CH_3CO_2H} Product$$

Reaction-2

$$CH_3CO_2Na \atop CH_3CO_2H} Product$$

$$CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop C$$



Which of the following is true about given graphs A and B?

(a) 
$$A \rightarrow S_{N^1} \quad B \rightarrow S_{N^2}$$
  
(c)  $A \& B \rightarrow E_1$ 

(b) 
$$A \rightarrow S_{N^2}$$
,  $B \rightarrow S_{N^1}$ 

(c) 
$$A \& B \rightarrow E$$

(d) 
$$A \& B \xrightarrow{N} E_2$$

30. In each of the following groups, which is the strongest (best) nucleophile?

(I) (1) 
$$H_3C - O^-$$

(3) 
$$H_3 C - S^-$$
 in  $CH_3OH$ 

31. 
$$\bigcirc \bigcup_{\substack{\parallel \\ 0}} - (CH_2)_4 - CH_2 - Cl \xrightarrow{\text{NaNH}_2 \atop \text{dimethoxy ethane}} (A); \text{ Product } (A) \text{ is } :$$

(c) 
$$CH_2$$
  $CH_2 - NH_2$ 

Which of the following reaction is an elimination reaction? 32.

(a) 
$$H$$
  $H_2SO_4$   $+ H$ 

(c) 
$$\xrightarrow{H}$$
  $\xrightarrow{\text{NaOCH}_3}$   $\xrightarrow{\text{OCH}_4}$ 

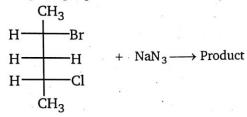
(d) both (a) and (b)

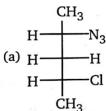
33. 
$$CH_2 - Cl \xrightarrow{CH_3OH(S_{N^1})} Product$$

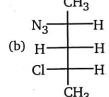
Which of the following products can be obtained from above reaction?

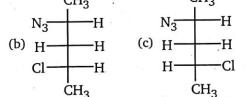
(a) 
$$CH_2 - OCH_3$$
 (b)  $CH_3O O$  (c)  $CH_3$  (d) All of these

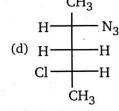
What is the principal product of the following reaction? 34.











What would be the effect of increasing solvent polarity on the rate of each of the following 35. reactions ? (Nu = neutral nucleophile)

(A) Nu + 
$$R - L \longrightarrow \overset{\oplus}{\text{Nu}} - R + L^{-}$$

- (b) decreases (a) increases
- (c) constant
- (d) can not be predicted

**(B)** 
$$R - L^{\oplus} \longrightarrow R^{\oplus} + : L$$

- (a) increases
- (b) decreases
- (c) constant
- (d) cannot predict

Which of the following is most reactive toward S  $_{\mathrm{N}^2}$  reaction ? 36.

(a) 
$$CH_2 = CH - CH_2 - Cl$$

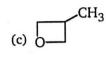
(b) 
$$Ph - CH_2 - Cl$$

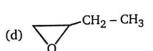
(d) 
$$Ph - C - CH_2 - Cl$$
 $\parallel$ 
O

4-chloro-1-butanol + NaOH  $\longrightarrow$  (B) 37. Product (B) of the above reaction is:









- **38.** In the given pairs of alkyl-halide, in which pair the first compound is more reactive than second compound toward  $S_{M^2}$  reaction?
  - (a)  $(CH_3)_2CHBr$  or  $CH_3-CH_2-CH_2-Br$
  - (b)  $CH_3 CH_2 CH_2 Br$  or  $CH_3 CH_2 CH_2 I$
  - (c) Ph Br or  $CH_3 CH_2 CH_2 Br$
  - (d)  $CH_2 = CH CH_2 Cl$  or  $H_2C = CH Cl$
- **39.** In the given pair of reaction in which pair the second reaction is more reactive than first toward  $S_{N^2}$  reaction?
  - (a)  $CH_3 CH_2 Cl + CH_3 CH_2 O^- \longrightarrow Et O Et$  (or)

$$CH_2 - CH_2 - Cl + CH_3 - CH_2 - OH \longrightarrow Et - O - Et$$

(b)  $CH_3 - CH_2 - Cl + EtO^- \longrightarrow Et - O - Et$  (or)

$$CH_3 - CH_2 - Cl + EtS^- \longrightarrow CH_3 - CH_2 - S - Et$$

(c)  $\operatorname{Et} - \operatorname{Cl} + \operatorname{CH}_3 \operatorname{O}^- \longrightarrow \operatorname{Et} - \operatorname{O} - \operatorname{CH}_3$  (or)

$$\underbrace{\text{Et} - \text{Cl} + \text{CH}_3\text{O}^-}_{(2\text{m})} \longrightarrow \text{Et} - \text{O} - \text{CH}_3$$

(d)  $Et - Br + Ph_3P \longrightarrow Et - PPh_3$  (or)

$$Et - Br + Ph_3N \longrightarrow E + -NPh_3$$

- **40.** Among the following pair of reactions in which pair the second reaction is more reactive than first in  $S_{N^1}$  reaction?
  - (a)  $Me_3CCl + H_2O \longrightarrow Me_3COH$
- (or)  $Me_3CBr + H_2O \longrightarrow Me_3COH$
- (b)  $Me_3CCl + CH_3OH \longrightarrow Me_3C \longrightarrow OCH_3$  (or)  $Me_3C \longrightarrow Cl + H_2O$



- (c)  $Me_3CCl+ H_2O \longrightarrow$  (or)  $Me_3CCl+ H_2O$ (2M)
- (d) All of these
- **41.** Which is a true statement concerning the transition state of an  $S_{N^2}$  reaction?
  - (a) Closely resembles a carbocation intermediate
  - (b) The electrophile is responsible for the reaction
  - (c) Lower is energy than the starting materials
  - (d) Involves both the nucleophile and electrophile
- **42.** Increasing the concentration of a nucleophile in a typical  $S_{N^2}$  reaction by a factor of 10 will cause the reaction rate to :
  - (a) increase by a factor of 10
- (b) increase by a factor of 102
- (c) decrease by a factor of 10
- (d) remain about the same
- **43.** Decreasing the concentration of an electrophile in a typical  $S_{N^2}$  reaction by a factor of 3 will cause the reaction ratio to :
  - (a) increase by a factor of 3
- (b) increase by a factor of 32
- (c) decrease by a factor of 3
- (d) remain about the same

44. Increasing the concentration of an electrophile in a typical  $S_{N^2}$  reaction by a factor of 3 and the concentration of the nucleophile by a factor of 3 will change the reaction rate to:

con act act act ac

- (a) increase by a factor of 6
- (b) increase by a factor of 9
- (c) decrease by a factor of 3
- (d) remain about the same
- 45. Consider the following reaction and select the best choice that represents the reaction.

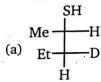
$$CH_3$$

$$Na^{\oplus -SCH_2CH_3} \rightarrow Product$$

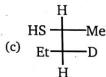
(c) 
$$CH_3$$
 $SCH_2CH_3$ 

$$(d) \begin{array}{c} CH_3 & CH_3 \\ & & \\ & & \\ H & \\ \end{array} S - CH_2CH_3$$

46.  $Et \xrightarrow{H} D \xrightarrow{KSH} Product; Identify the product.$ 



$$\begin{array}{ccc}
 & H \\
 & Me & H \\
 & Et & D
\end{array}$$



$$(d) \xrightarrow{Et} D$$

47. The reaction,

$$H_{III}OH + SOCl_2 \longrightarrow H_{III}Cl + SO_2 + HCl$$

proceeds by the..... mechanism.

- (a) S<sub>N</sub>i
- (b) S<sub>N<sup>2</sup></sub>
- (c) S<sub>E2</sub>
- (d) S<sub>N1</sub>

48. Consider the following anions.

$$CF_3 - S - O^ C_6H_5 - S - O^ C_6H_5 - S - O^ CH_3 - C - O^ CH_3 - C - O^ CH_3 - C - O^-$$

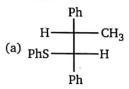
When attached to  $sp^3$ -hybridized carbon, their leaving group ability in nucleophilic substitution reaction decreases in the order :

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

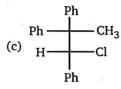
49.  $Cl \xrightarrow{Ph} H \xrightarrow{Ph SNa} Principal organic product of the reaction will be :

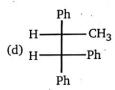
Ph

<math>S_{N^2}$ 



$$\begin{array}{c|c}
 & Ph \\
 & H \longrightarrow CH_3 \\
 & H \longrightarrow SPh \\
\end{array}$$





- **50.** Reaction of *R*-2-butanol with *p*-toluenesulphonyl chloride in pyridine followed by reaction with LiBr gives:
  - (a) R-2-butyl bromide

(b) S-2-butyl tosylate

(c) R-2-butyl tosylate

- (d) S-2-butyl bromide
- **51.** The compound which undergoes  $S_{N^1}$  reaction most rapidly is:
  - (a) Br

(b) Br

(c)  $\sim$  CH<sub>2</sub>Br

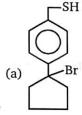
- (d) Br
- 52. Addition of KI accelerates the hydrolysis of primary alkyl halides because:
  - (a) KI is soluble in organic solvents
  - (b) the iodide ion is a weak base and a poor leaving group
  - (c) the iodide ion is a strong base
  - (d) the iodide ion is a powerful nucleophile as well as a good leaving group
- **53.** Which of the following phrases are not correctly associated with  $S_{N^1}$  reaction?
  - (1) Rearrangement is possible
  - (2) Rate is affected by polarity of solvent
  - (3) The strength of the nucleophile is important in determining rate
  - (4) The reactivity series is tertiary > secondary > primary
  - (5) Proceeds with complete inversion of configuration
  - (a) 3, 5

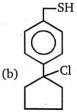
(b) 5 only

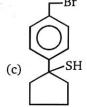
(c) 2, 3, 5

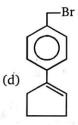
(d) 3 only

54. 
$$\underbrace{ \begin{array}{c} \text{CH}_3 \\ \text{SO}_2\text{Cl}_2 \\ h\nu \end{array}} (A) \xrightarrow{\text{NBS}} (B) \xrightarrow{\text{KSH}} (C) \text{, Product } (C) \text{ is :}$$

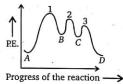








**55.** Energy profile diagram for an exothermic reaction,  $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$ , is given below.



The rate determining step of the reaction is :

(a) 
$$A \longrightarrow B$$

(b) 
$$B \longrightarrow C$$

(c) 
$$C \longrightarrow L$$

(d) can not predict

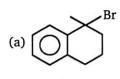
56. 
$$(A)$$

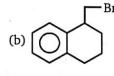
NBS

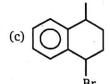
(A)

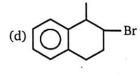
Major

Major product is (A) is:







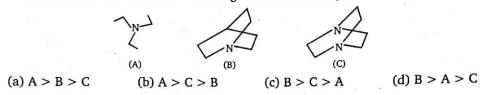


 $\underset{S_{N^2} \text{ conditions}}{\text{LiBr/DMSO}} \text{Major product } (X)$ 

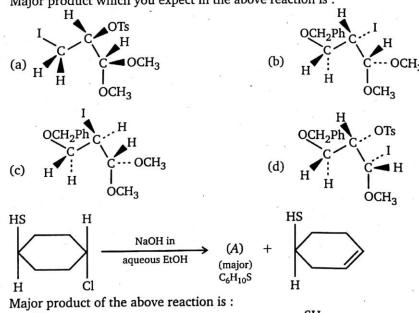
The product X is:

60.

Relative rate of reaction of the following amine with methyl iodide is: 58.



Major product which you expect in the above reaction is:



61. 
$$CH_3 - C - C^{14} - CH_3 \xrightarrow{\Delta} Major product of the reaction is: CH3 OTs$$

(a) 
$$CH_3 \sim C = C < CH_3$$

(b) 
$$CH_3 - CH_2 = CH_2$$
  
 $CH_2 = CH_2$ 

(c) 
$$CH_3$$
  $C = C$   $CH_3$ 

(d) 
$$CH_3$$
  $C = C$   $CH_3$   $C = C$ 

62. The decreasing order of reactivity of the compounds given below towards solvolysis under identical conditions is:

$$CH_{3} - C - CH_{3} \qquad CH_{3} - C - CH_{3}$$

$$(I) \qquad (II) \qquad (III)$$

$$CH_{3} - C - CH_{3}$$

(a) 
$$II > III > I$$

(b) 
$$I > II > III$$

(c) 
$$III > II > I$$

$$II < I < II$$
 (b)

63. OH 
$$\frac{1. \text{One Eq. NaOH}}{2 \text{ MeBr}} (A); \text{ Product } (A) \text{ is :}$$

- (d) None of these
- (R)-2-octyl tosylate is solvolyzed in water under ideal  $S_{N^1}$  conditions. The product(s) will 64.
  - (a) R-2-octanol and S-2-octanol in a 1:1 ratio
  - (b) R-2-octanol and S-2-octanol in a 1.5:1 ratio
  - (c) R-2-octanol only
  - (d) S-2-octanol only

- **65.** From each of the following pairs select the compound that will react faster with sodium iodide in acetone:
  - Pair-A: (1) 2 Chloropropane
- (2) 2- Bromopropane
- Pair-B: (3) 1 Bromobutane
- (4) 2- Bromobutane

- (a) 1,3
- (b) 1,4
- (c) 2,3
- (d) 2,4
- **66.** Among the given halides, which one will give same product in both  $S_{N^1}$  and  $S_{N^2}$  reactions.
  - (I) CH<sub>3</sub> CH CH<sub>2</sub> CH CH<sub>3</sub>

    Br
- (II) Cl CH<sub>3</sub>

(III) Cl

(IV) CH<sub>3</sub> -CH - Br

- (a) (III) only
- (b) (I) & (II)
- (c) (III) & (IV)
- (d) (I), (III) & (IV)

- **67.** Product(s) formed during this reaction is/are:
  - $CH_2 \overline{C}H_2 OTs$   $\overline{C}H_2 CH_2 OAc$
- $\xrightarrow{\text{AcONa}} \text{Product ? [ C}^* = \text{isotopic carbon]}$
- $CH_2 \overset{*}{C}H_2 OTs$
- (b)  $CH_2 \mathring{C}H_2 OAc$

(c) OAc

- (d) Both (a) & (b)
- **68.** Anisole  $\xrightarrow{\text{excess HI (conc.)}} \text{Product}$ 
  - (a)  $\langle O \rangle$  + CH<sub>3</sub>I
- (p) (D)—I + CH3OH
- (c) OH + CH<sub>3</sub>I
- (d) OH + CH<sub>3</sub>CH<sub>2</sub>I
- **69.** Which of the following compounds would react faster with NaCN in an  $S_{N^2}$  reaction?
  - (a) J
- (b) OT:
- (c) MeO
- (d)  $\sim$ OTs

70. HC 
$$\equiv$$
 CNa + Cl - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - I  $\longrightarrow$  (A); Major product (A) is:

- (a)  $H C \equiv C CH_2 CH_2 CH_2 I$
- (b)  $CH_2 = CH CH_2 I$
- (c)  $H C \equiv C CH_2 CH_2 CH_2 CI$
- (d)  $CH_2 = CH CH_2 Cl$
- 71. What is the major product obtained in the following reaction?

$$\sim$$
 SNa + CH<sub>3</sub> — Br  $\xrightarrow{\text{Et}_2\text{O}}$  Product

- (a)
- (b) Br
- (c)  $\sim$  S<sub>CH<sub>3</sub></sub> (d)  $\sim$
- 72. Br  $CH_3 + OH^- \xrightarrow{S_{N^2}} A$ ; The product A is:
  - (a) HOCH<sub>3</sub>

- (b) HO CH<sub>3</sub>
- (c) Both (a) and (b) are correct
- (d) None is correct
- **73.**  $Me_2C = CH CH_2 CH_2 CI \xrightarrow{H_2O} (X)$ ; Major product of the reaction is :

(b) 
$$Me_2C = CH - CH_2 - CH_2 - OH$$

(c)  $Me_2C = CH - CH - CH_2 - OH$ 

74.  $OH \xrightarrow{HBr \atop \Delta} (A)$ 

$$OH \xrightarrow{\text{HBr}} OB$$

$$OCH_3$$

Product (A) and (B) respectively are:

(a) 
$$OH$$
 and  $OH$  (b)  $OH$  and  $OH$   $OH$   $OH$ 

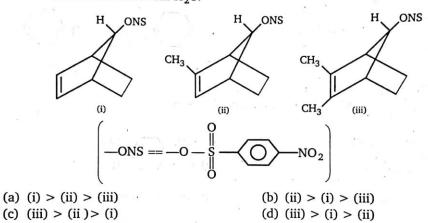
#### 280

# ORGANIC Chemistry for IIT-JEE

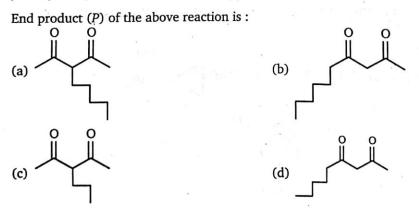
(c) 
$$OH$$
 and  $OH$  (d)  $OH$  and  $OCH_3$   $OCH_3$ 

**75.** Relative rate of reaction with  $H_2O$ .

00,00,00,00



76.  $\frac{2 \text{ eq. KNH}_2}{\text{NH}_3(l)} \xrightarrow{\text{n-C}_4\text{H}_9-\text{Br} \atop \text{then H}_3\text{O}^{\oplus}} (P)$ 



77. Which of the following statements is correct regarding the rate of hydrolysis of the compounds (A) and (B) by  $S_{N^1}$  reaction?

$$A$$
 Br  $O$   $B$ 

- (a) A reacts faster than B
- (b) B reacts faster than A
- (c) Both A and B reacts at the same rate
- (d) Neither A nor B reacts
- **78.** What are reactant X and product Y in the following sequence of reactions?

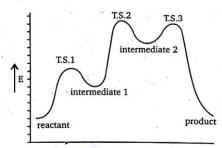
**79.** Transition state of given  $S_{N_2}$  is:

$$(a) \begin{bmatrix} \delta \Theta \\ OR \\ OR \\ H \\ Br \\ \delta \Theta \end{bmatrix}^{\ddagger} \qquad (b) \begin{bmatrix} CH_2 - O - R \\ OR \\ OR \\ H \\ Br \\ \delta(+) \end{bmatrix}^{\ddagger}$$

(c) 
$$\begin{bmatrix} \delta \oplus & \\ OR & \\ & H \\ & Br \\ \delta \ominus & \end{bmatrix}$$

(d) 
$$\begin{bmatrix} \delta(-) \\ OR \\ H \\ Br \\ \delta(-) \end{bmatrix}^{\ddagger}$$

- **80.**  $C_6H_{13}Br + OH^- \longrightarrow C_6H_{13}OH + Br^-$  is an example of:
  - (a) Nucleophilic addition
- (b) Nucleophilic substitution
- (c) Electrophilic addition
- (d) Electrophilic substitution
- (e) Free radical substitution
- **81.** Transition state 2 is structurally most likely as:

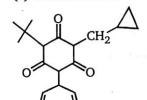


(a) intermediate 1

(b) transition state 3

(c) intermediate 2

(d) product



x = Number of aromatic compound obtained when above compound undergo complete acidic hydrolysis.

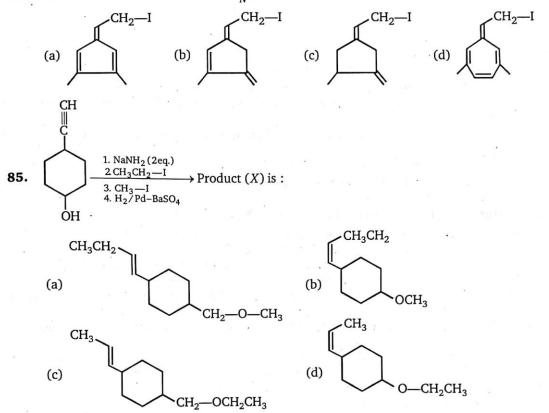
(a) 1

82.

- (b) 2
- (c) 3
- (d) 4

- 83.  $S_N 1$  and  $S_N 2$  reactions are
  - (a) Both stereospecific
  - (b) Both stereoselective
  - (c) Stereoselective and stereospecific respectively
  - (d) Stereospecific and stereoselective respectively

**84.** Most reactive compound toward  $S_{N^1}$  is :



						ANSV	VERS	— LE	VEL 1						
1.	(a)	2.	(b)	3.	(c)	4.	(a)	5.	(b)	6.	(b)	7.	(b)	8.	(d)
9.	(b)	10.	(a)	11.	(c)	12.	(a)	13.	(d)	14.	(d)	15.	(b)	16.	(c)
17.	(a)	18.	(a)	19.	(c)	20.	(d)	21.	(b)	22.	(a)	23.	(c)	24.	(c)
25.	(d)	26.	(d)	27.	(d)	28.	(a)	29.	(a)	30.	(d)	31.	(b)	32.	(d)
33.	(d)	34.	(c)	35.	A(a)	35.	B(b)	36.	(d)	37.	(b)	38.	(d)	39.	(b)
40.	(d)	41.	(d)	42.	(a)	43.	(c)	44.	(b)	45.	(c)	46.	(d)	47.	(a)
48.	(b)	49.	(b)	50.	(d)	51.	(b)	52.	(d)	53.	(a)	54.	(b)	55.	(a)
56.	(a)	57.	(b)	58.	(c)	59.	(c)	60.	(b)	61.	(c)	62.	(d)	63.	(a)
64.	(b)	65.	(c)	66.	(d)	67.	(d)	68.	(c)	69.	(d)	70.	(c)	71.	(c)
72.	(b)	73.	(d)	74.	(b)	75.	(c)	76.	(d)	77.	(b)	78.	(b)	79.	(d)
80.	(b)	81.	(c)	82.	(b)	83.	(b,c)	84.	(d)	85.	(b)				



1. Statement-1: Nucleophilicity order in polar-protic solvent is  $I^- < Br^- < Cl^- < F^-$ 

**Statement-2**: Due to bigger size of I<sup>-</sup> it is less solvated in polar-protic solvent.

- (a) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (b) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (c) Statement-1 is true, statement-2 is false.
- (d) Statement-1 is false, statement-2 is true.

# 2. Statement - 1 : $CH_3 - CH_2 - Cl + NaI \xrightarrow{Acetone} CH_3 - CH_2 - I + NaCl \downarrow$

**Statement- 2:** Acetone is polar-protic solvent and solubility order of sodium halides decreases dramatically in order NaI > NaBr > NaCl. The last being virtually insoluble in this solvent and a 1° and 2° chloro alkane in acetone is completely driven to the side of Iodoalkane by the precipitation reaction.

- (a) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for statement-1.
- (b) Statement-1 is true, Statement-2 is true and Statement-2 is Not the correct explanation for statement-1.
- (c) Statement-1 is true, Statement-2 is false.
- (d) Statement-1 is false, Statement-2 is true.
- 3. Encircle whichever of the following:
  - (a) is the stronger nucleophile (aprotic solvent): F or I
  - (b) is the stronger nucleophile (protic solvent): F or I
  - (c) is the stronger base: For I
  - (d) is the stronger nucleophile (protic solvent): NH3 or NH2NH2
  - (e) is the better leaving group : CH<sub>3</sub>COO or CH<sub>3</sub>SO<sub>3</sub>
- 4. Encircle whichever of the following:

(a) undergoes an 
$$S_{N^2}$$
 reaction more rapidly,  $CH_3 - Br$  or  $CH_3 - CH - CH_3$ 

(b) undergoes an  $S_{N^1}$  reaction more rapidly,  $CH_3 - Br$  or  $CH_3 - CH - CH_3$ 

(c) undergoes an 
$$E_2$$
 reaction to give (Z)-1,2-diphenylpropene:

# (d) reacts with NaI to give (Z)-1,2-diphenylpropene :

(e) undergoes an  $S_{N^1}$  reaction more rapidly,

### **5.** Encircle whichever of the following:

(a) undergoes an  $S_{N^2}$  reaction more rapidly:  $CH_2$ -Br or  $CH_2$ -Br

(b) undergoes an 
$$E_1$$
 reaction more rapidly :  $\begin{array}{c} CH_3 \\ CH-CH_2-CH_2 \\ Br \end{array}$  or  $\begin{array}{c} CH_3 \\ C-CH_2-CH_3 \\ Br \end{array}$ 

(c) undergoes an  $S_{N^1}$  reaction more rapidly:

(d) undergoes an  $S_{N^2}$  reaction more rapidly:

(e) undergoes an  $\rm E_2$  reaction more rapidly :

$$\int_{Cl} \text{or} \int_{C} C$$

# 6. Match the column:

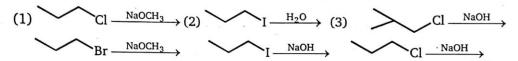
	Alkyl halide		Relative ra	ate	Relative rate (S <sub>N<sup>2</sup></sub> )
(a)	CH <sub>3</sub> – Br	(p)	1	(w)	1200
(b)	CH <sub>3</sub> -CH <sub>2</sub> - Br	(q)	1.05	(x)	40
(c)	CH <sub>3</sub> -CH -Br	(r)	11	(y)	16
(d)	$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{CH}_3 - \text{C} - \text{Br} \\ \mid \\ \text{CH}_3 \end{array}$	(s)	1,200000	(z)	1

# 7. Matrix:

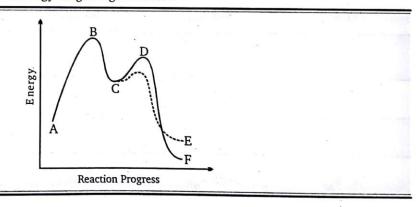
	Column (I)		Column (II)	
	Compound	Type of reaction		
(a)	CI CI	(p)	S <sub>N</sub> <sup>1</sup> reaction can take place	
(b)	CI	(q)	S <sub>N<sup>2</sup></sub> reaction can take place	
(c)	CI	(r)	$S_{N^1}$ is not possible	
(d)	CI	(s)	S <sub>N<sup>2</sup></sub> is not possible	

#### ALKYL HALIDES (SUBSTITUTION)

- 8. Encircle whichever of the following:
  - (a) undergoes an  $S_{N^2}$  reaction more rapidly, O
  - (b) undergoes an S  $_{N^1}$  reaction more rapidly,  $(CH_3)_3C-Br$  or  $(CH_3)_3C-I$
  - (c) undergoes an  $S_{N^1}$  reaction more rapidly, P or P or
- **9.** Reactivity: Circle the reaction that reacts FASTER by  $S_{N^2}$  in each pair:



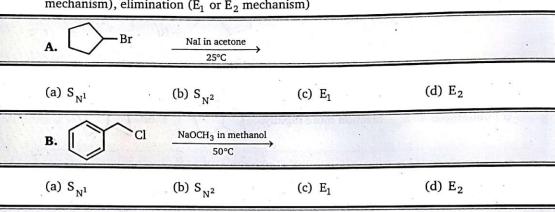
10. Consider the potential energy diagram given below

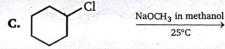


- (X) Name the positions A-D
- (Y) Answer the following questions.
  - (i) Both reaction pathways are: EXOTHERMIC or ENDOTHERMIC
  - (ii) Which step is the rate determining step (RDS)?
    - B or D
  - (iii) Which product is most stable?

- E or F
- (iv) In accordance with Hammonds postulate, exothermic reactions tend to have
  - (a) early transition states that are reactant like
  - (b) late transition states that are reactant-like
  - (c) early transition states that are product-like
  - (d) late transition states that are product-like.

11. Select whether the following combinations of reactants will react by substitution (S $_{N^1}$  or S $_{N^2}$  mechanism), elimination (E $_1$  or E $_2$  mechanism)





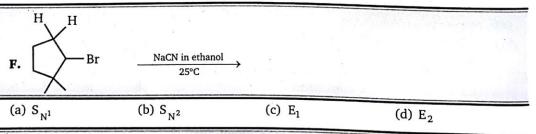
(a) 
$$S_{N^1}$$
 (b)  $S_{N^2}$ 
**D.**  $(CH_3)_3C - OH \xrightarrow{BBr 48\% \text{ in } H_2O}$ 

- (a)  $S_{N^1}$  (b)  $S_{N^2}$ 
  - (b)  $S_{N^2}$  (c)  $E_1$  (d)  $E_2$

(c) E<sub>1</sub>

- E.  $(CH_3)_2CH Br$ NaCN in ethanol
  25°C
- 25°C
- (a)  $S_{N^1}$  (b)  $S_{N^2}$
- (c) E<sub>1</sub>
- (d) E<sub>2</sub>

(d) E<sub>2</sub>



- **G.**  $(CH_3)_2CHCH_2CH_2 OH$  HBr 48% in  $H_2O$  50°C
- (a) S<sub>N1</sub>
- (b)  $S_{N^2}$
- (c) E<sub>1</sub>
- (d) E<sub>2</sub>

#### ALKYL HALIDES (SUBSTITUTION)

**12.** Examine the ten structural formulas shown in fig. & select that satisfy each of the following conditions. Write one or more (a through j) in each answer box.

(a)	Br	(ъ)	$\begin{array}{c} \operatorname{CH}_3 \\ \mid \\ \operatorname{H}_3\operatorname{C} - \operatorname{C} - \operatorname{Cl} \\ \mid \\ \operatorname{CH}_3 \end{array}$	(c)	CH <sub>2</sub> – Br
(d)	CH <sub>3</sub> –I	(e)	CH <sub>2</sub> – Br	<b>(f)</b>	CI
(g)	$\begin{array}{c} \operatorname{CH_3} \\ \operatorname{H_3C} - \operatorname{C} - \operatorname{CH_2} - \operatorname{Cl} \\ \operatorname{CH_3} \end{array}$	(h)	$\begin{array}{c} {\rm H_2C} {\rm CH_2-CI} \\ {\rm CH_3} \end{array}$	(i)	Br
(j)	Cl				

- A. Which compounds give an  $S_{N^2}$  substitution reaction on treatment with alcoholic NaSH?
- **B.** Which compounds give an E<sub>2</sub> elimination reaction on treatment with alcoholic KOH?
- C. Which compounds do not react under either of the previous reaction conditions?

13. Select which reaction from the following reaction pairs will occur faster.

Select Which	reaction from the following reaction pairs will occur faster.
	PART - 1
Reaction A	$CH_3 \xrightarrow{H_2O} CH_3$
Reaction B	$ \begin{array}{c} I \\ H_{2O} \\ \hline DMSO \end{array} $ $ \begin{array}{c} OH \\ H \end{array} $
	PART - 2
Reaction C	$Cl$ $CH_3 \xrightarrow{Nal} CH_3$
Reaction D	$CH_2CI \longrightarrow CH_2I$ $\xrightarrow{NaI} \longrightarrow DMSO$
	PART - 3
Reaction E	$ \begin{array}{c c} I & & Cl \\ H & \underline{\text{NaCl}} & & H \end{array} $
Reaction F	$\begin{array}{c c} I & & \\ H & \xrightarrow{NaCl} & H \end{array}$
	PART - 4
Reaction G	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
Reaction H	$\begin{array}{c} \text{Br} \\ \text{H} & \xrightarrow{\text{NaN}_3} \\ \text{DMSO} \end{array}$

	PART - 5
Reaction I	$\begin{array}{c c} CH_2-CI & CH_2-I \\ \hline & \\ \hline \end{array}$
Reaction J	$ \begin{array}{c c} \text{Br} & I \\ \hline \\ NaI \\ \text{acetone} \end{array} $ $ \begin{array}{c} \text{CH}_3 \end{array} $ $ \begin{array}{c} \text{CH}_3 \end{array} $

## 14. Tick your answer in the given box.

	Alkyl Halide	2-D Structure	Expect S <sub>N</sub> <sup>2</sup> (at a reasonable rate)
(a)	1-Bromobutane	Br	Yes
(b)	1- Chlorobutane	CI	Yes
(c)	2-Bromobutane	Br	Yes
(d)	2-Chlorobutane	CI	Yes
(e)	2-Chloro-2-methyl propane	CI	Yes

(f)		Br	Yes
	Bromocyclohexane		No
(-)		Br	Yes
(g)	Bromobenzene		No
(h)	Benzyl bromide	CH <sub>2</sub> -Br	Yes
		0	No
(i)	1-Bromo-2,2-dimethyl propane	Br	Yes
		~\	No
Ø	District the second		Yes
U)	Bicyclo compound	Br	No
(k)	1-bromotriptycene	Br	Yes
(AL)	1-ыонопрусене		No

#### 15. Match the column

	Column-I		Column-II
(a)	CI	(p)	It will undergo Nucleophilic Substitution reaction
(ъ)	CH <sub>2</sub> —Cl	(q)	It will undergo $E_2$ reaction
(c)	CH <sub>3</sub> C—Cl	(r)	It will undergo $E_1$ reaction
(d)	NO <sub>2</sub>	(s)	It will undergo $S_{N^2}$ reaction
		(t)	It will undergo $S_{N^1}$ reaction

16.

17.

marks and	Column (I)		Column (II)
(a)	$Ph \xrightarrow{\qquad} Cl \xrightarrow{\qquad H_2O \qquad}$	(p)	$S_{N^1}$
(b)	$\sim$	(q)	$S_{N^2}$
(c)	$ \begin{array}{c}                                     $	(r)	Carbocation is intermediate
(d)		(s)	Carbanion is intermediate

18.

	Column (I)		Column (II)
	(Reaction sequence)		(Reagent required)
(a)	$\rightarrow$ OEt	(p)	EtO <sup>⊖</sup>
(b)	$\rightarrow$ Br $\rightarrow$	(q)	EtBr
(c)	$\rightarrow$ OEt	(r)	EtOH∕H <sup>⊕</sup>
(d) E	$Et - Cl \longrightarrow /$	(s)	Et-Cl/Na ether

ALKYL HALIDES

295

**19.** Choose the one compound within each set that meets the indicated criterion :

	Column (I)	A Death	Column (II)
(a)	The compound that reacts with alcoholic KOH to liberate Halide ion through substitution reaction.	(p)	$O_2N$ $CH_3$
(b)	The compound that cannot be prepared by a Williamson ether synthesis.	(q)	$\bigcirc$ OC <sub>2</sub> H <sub>5</sub>
(c)	The compound that gives an acidic solution when allowed to stand in aqueous ethanol.	(r)	o
(d)	The ether that cleaves more rapidly in HI.	(s)	$ \begin{array}{c}  & \text{Br} \\  & \text{I} \\  & \text{C} \\  & \text{CH}_3 \end{array} $

#### ANSWERS -

- 1.
- c The reaction is Finkelstein reaction. 2.

- (b)  $(\Gamma)$ ; (c)  $(\Gamma)$ ; (d)  $(NH_2-NH_2)$
- (e) CH<sub>3</sub>SO<sub>2</sub>

- (a) CH<sub>3</sub> -Br
- (b) CH<sub>3</sub> -CH-CH<sub>3</sub>
- (c)

- a p, w; b q, x; c r, y; d s, z
- a-r, s; b-p, q; c-r, s; d-r, s



- 9.

- (X) A- reactants, B-transition state, C-Inter mediate, D- transition state 10.
  - (Y) (i) exothermic (ii) B (iii) F (iv) a

**11.** A - b; B - b; C - d; D - a; E - b; F - b; G - b

**12.** 
$$A - c$$
,  $d$ ,  $e$ ,  $f$ ,  $h$ ;  $B - b$ ,  $c$ ,  $f$ ,  $i$ ;  $C - a$ ,  $g$ ,  $j$ 

**14.** Yes – a, b, c, d, f, h, 
$$No - e$$
, g, i, j, k

17. 
$$a-p, r$$
;  $b-q$ ;  $c-s$ ;  $d-r$ 

**18.** 
$$a-q$$
;  $b-p$ ;  $c-r$ ;  $d-q$ 

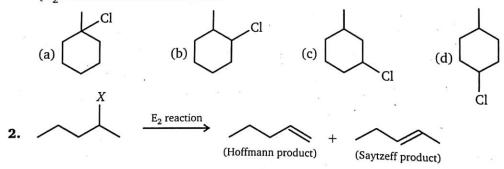
19. 
$$a-p$$
;  $b-r$ ;  $c-s$ ;  $d-q$ 

# Elimination Reactions $(E_1, E_2, E_{1CB}, E_i)$

# 

1. Which of the following alkyl halide gives only one product (excluding stereoisomer) when undergo  $E_2$  reaction ?

 $(E_2 = elimination bi-molecular)$ 



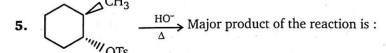
- (A)In the above reaction, maximum Saytzeff product will obtained when:
- (a) X = -I
- (b) X = -Cl
- (c) X = -Br
- (d) X = -F
- **(B)** In the above reaction Hoffmann product is major when X is:
- (a) -I
- (b) Cl
- (c) Br
- (d) F

3. 
$$0 \qquad N-H^{(P)}$$

when (P) undergoes Hoffmann exhaustive methylation (twice) then the product obtained will be:

Product (A) & (B) of the above reaction is:

- (a) A = P, B = P
- (b) A = Q, B = Q
- (c) A = P, B = Q
- (d) A = Q, B = P





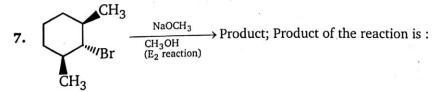




6. Which of these dehydrates most easily?

(a) 
$$CH_3 - CH_2 - CH_2 - OH$$

(d) 
$$CH_3 \stackrel{|}{-}C - CH_2 - OH$$
  
 $CH_3$ 

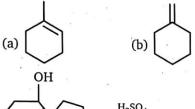






(d) No reaction

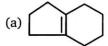
Major product A is:

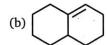


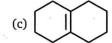
(c)

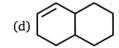
9.

Major product A is:









In which of the following reaction Saytzeff alkene is major product? 10.

(a) 
$$\text{CH}_3$$
 –  $\text{CH}_2$  –  $\text{CH}_2$  –  $\text{CH}_3$  –

(b) 
$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{EtO^-} \Delta$$

(c) 
$$CH_3 - CH_2 - C - CH_3 \xrightarrow{t-BuOK} \Delta$$

(c) 
$$CH_3 - CH_2 - C - CH_3 \xrightarrow{t-BuOK} \Delta$$
 (d)  $CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{CH_3OK} \Delta$ 

 $\begin{array}{c|c} CH_3 \\ Ph & & H \\ \hline Ph & & Br \end{array} \xrightarrow{alc. \ KOH} Major \ product \ of \ the \ reaction \ is : \end{array}$ 

(a) 
$$Ph C = C CH_3$$
 $CH_3$ 

(b) 
$$CH_3$$
  $C = C$ 

(c) 
$$CH_3$$
  $C = C$   $CH_2$ 

$$\begin{array}{c|c} \operatorname{Ph}-\operatorname{CH}-\operatorname{CH}-\operatorname{Ph} \\ | & | \\ \operatorname{CH}_3 & \operatorname{OH} \end{array}$$

- The conversion of 2, 3-dibromobutane to 2-butene with Zn is: 12.
  - (a) Redox reaction

(b) α-Elimination

(c) β-Elimination

(d) Both  $\alpha$ -elimination and redox reaction

13. 1, 3-Dibromopropane is heated with zinc dust in ether. The product formed is :

(a) propene

(b) propane

(c) cyclopropane

(d) 3-bromopropane

14. Reaction (1)  $\xrightarrow{\text{Br}}$   $\xrightarrow{\text{alc. KOH}}$  (A) (major)

Reaction (2)  $\xrightarrow{\text{Rr}}$   $\xrightarrow{\text{alc. KOH}}$  (B) (major)

Reaction (3)  $\xrightarrow{\text{Br}}$   $\xrightarrow{\text{alc. KOH}}$  (C) (major)

Product obtained in above reactions (1), (2) & (3) is:

- (a) A = B but C is different
- (b) A = C, but B is different
- (c) B = C, but A is different
- (d) A = B = C all product are identical

> Reaction (3) Cl  $\stackrel{Cl}{\underset{Cl}{\longrightarrow}}$   $\stackrel{\text{""Cl}}{\underset{Cl}{\longrightarrow}}$   $\stackrel{\text{3 mole alc. KOH}}{\longrightarrow}$  (C)

Product obtained in above reactions (1), (2) & (3) is:

(a) A = B, C is different

(b) A = C, B is different

(c) B = C, A is different

(d) A = B = C is same

16. 
$$\xrightarrow{\text{alc. KOH}}$$
  $(x)$ 
 $x \text{ is number of } E_2 \text{ product obtained (including stereoisomers)}$ 

Find (x).

(a) 3 (b) 4 (c) 5 (d) 6

$$CH_3$$
 $CH_3$ 
 $CH_$ 

Major product (A) is:

**18.** Which one of the following compound will be least susceptible to elimination of hydrogen bromide?

(a) 
$$Br - CH_2 - CH_2 - NO_2$$
 (b)  $Br - CH_2 - CH_2 - CH_3$  (c)  $Br - CH_2 - CH_2 - CN$  (d)  $Br - CH_2 - CH_2 - CO_2Et$ 

19. Two alkenes, X(91% yield) and Y(9% yield) are formed when the following compound is heated.

$$\begin{array}{c}
 & \xrightarrow{\text{CH}_3} & \xrightarrow{\Delta} X + Y \\
 & \text{N(CH}_3)_3 \text{OH} & \xrightarrow{91\%} 9\%
\end{array}$$

The structures of X and Y, respectively are:

(a) 
$$CH_3$$
 and  $CH_2$  (b)  $CH_3$  and  $CH_3$  (c)  $CH_3$  and  $CH_3$  (d)  $CH_3$  and  $CH_2$ 

**20.** In the dehydrohalogenation of 2-bromobutane; which conformation leads to the formation of *cis*-2-butene?

(a) 
$$H$$
 $CH_3$ 
 $CH_3$ 

21. 
$$O - H \longrightarrow O \\ CH_3 - C - Cl (2 \text{ mole}) \\ Pyridine \longrightarrow (A) \longrightarrow (B) + CH_3CO_2H$$

Product (B) of given reaction is:







22. What product will be formed from Hoffmann exhaustive methylation of following compound?

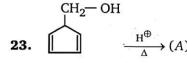
Me<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>Me 
$$\xrightarrow{\text{(i) CH}_3-\text{I (excess)}}$$
 Product  $\xrightarrow{\text{(ii) Ag}_2O}$ 

(a)  $Me - CH = CH_2$ 

(b)  $H_2C = CH_2$ 

(c)  $CH_3 - C = CH_2$  $CH_3$ 

(d)  $CH_3 - CH - CH = CH_2$ |
Me



Product (A) is:



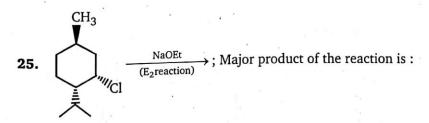


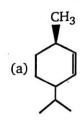


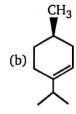


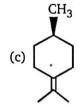
24. 
$$\xrightarrow{H^{\oplus}}_{\Delta}$$
; Products obtained are :

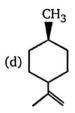
- (a) Racemic
- (b) Diastereomers
- (c) G.I
- (d) Positional isomers



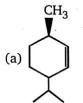


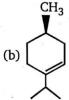


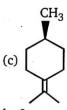


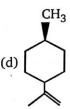


26.  $CH_3$   $Cl \xrightarrow{NaOEt}$ ; Major product of the reaction is:

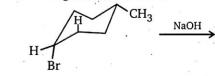


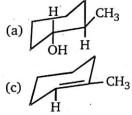






**27.** The  $E_2$  product of the following reaction will be ?



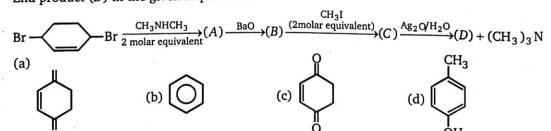


28. An halide C<sub>5</sub>H<sub>11</sub>Br on treatment with alc. KOH give 2-pentene only. The halide will be:

(a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - Br$$

(b) 
$$CH_3 - CH_2 - CH_2 - CH - CH_3$$

**29.** End product (D) in the given sequence is:



For each of the following pairs of  $E_2$  reaction, select the one that occurs with the greater rate constant.

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CI} + \text{CH}_3 - \text{C} - \text{O}^- \\ | \\ \text{CH}_3 \end{array}$$

(3) 
$$H_3C - CH - CH_3 + CH_3O^-$$
  
|  
Br

- (a) 2, 4, 6
- (c) 2, 3, 5

(d) 2, 4, 5

x and y mole consumed.

Value of 
$$x + y =$$

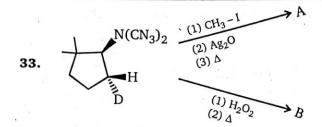
- (a) 5
- (b) 6
- (c) 7
- (d) 8
- The following bimolecular elimination reaction (E2) is carried out with different halogen leaving groups. The per cent yield of the two products (2-hexene and 1-hexene) for each leaving group is listed below.

$$+ CH_3O^- \xrightarrow{E_2} +$$

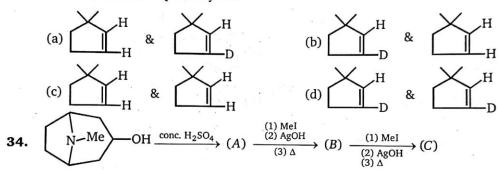
Leaving group	Conj. Acid pK <sub>a</sub>	%-yield of 2-hexene	%-yield of 1-hexene
X = I	- 10	81%	19%
X = Br	<b>-9</b>	72%	28%
X = C1	-7	67%	33%
X = F	3.2	30%	70%

Which of the following statement is (are) true concerning this series of  $E_2$  reactions?

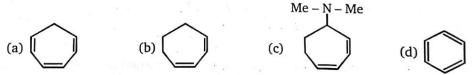
- (a) Based on the  $pK_a$ 's of the conjugate acid,  $I^-$  is the best leaving group and  $F^-$  is the poorest leaving group
- (b) When I-, Br and Cl are used as leaving groups, Zaitsev's rule is followed
- (c) F is the strongest base (and therefore the poorest leaving group) and the transition state for reaction with fluoride as the leaving group has the least double bond character
- (d) a, b, c are true



Product (A) & (B) respectively are :



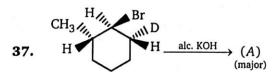
Product in above reaction is:



- 35. Major product obtained in the reaction of 1-phenyl-2-bromobutane with NaOMe is:
  - (a) (E)-1-phenylbut-1-ene
- (b) (E)-1-phenylbut-2-ene
- (c) 1-phenyl-2-ethoxybutane
- (d) (Z)-1-phenylbut-2-ene
- **36.** Which of the following alkyl halides give most complex mixture of alkene in an  $E_2$  reaction?

(a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - Br$$

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



Product (A) is:

Sum of number of  $\alpha$ -hydrogen present is compound A + B is:
(a) 18
(b) 19
(c) 20
(d) 21

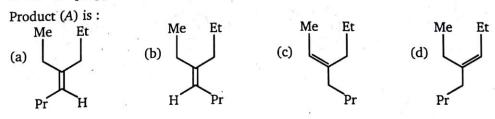
Identify A:

(a) 
$$\bigcap_{H}$$
 (b)  $\bigcap_{H}$  (c)  $\bigcap_{H}$  (d)  $\bigcap_{H}$  Br

**40.** 
$$CH_3 - CH_2 - C - CH_2 - Et \xrightarrow{alc. KOH} (A)$$

$$CH_2(n - Pr)$$

n - Pr = n - propyl



Ph
OH
$$\xrightarrow{H_3PO_4} OH$$

$$\xrightarrow{\Delta} Major product obtained by dehydration of given alcohol is:$$

42. Br NaOCH<sub>3</sub>(2mole) 
$$(A) \xrightarrow{\text{H}_3O^{\oplus}} (B)$$

Product (B) of above reaction is:

(a) 
$$OH$$
 (b)  $OH$  (c)  $OH$   $OH$   $OH$   $OH$   $OH$ 

43. Ph — CH— CH<sub>2</sub> — CH<sub>2</sub> 
$$\xrightarrow{Zn-Cu}$$
 Produc  
Br Br

Product of the above reaction is:

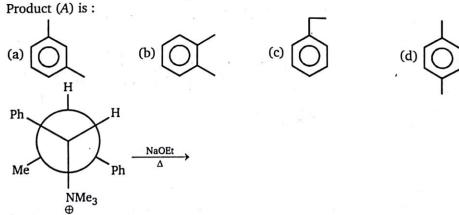
(a) 
$$Ph - CH = CH - CH_2 - Br$$
  
(c)  $PH - CHBr - CH = CH_2$ 

(c) 
$$PH - CHBr - CH = CH_2$$

(d) 
$$Ph - C \equiv C - CH_3$$

44. 
$$OH \xrightarrow{H^{\oplus}} (A)$$

45.



Major product of the above reaction is:

(a) 
$$Ph$$
  $C = C < Ph$ 

(b) 
$$Ph$$
  $C = C$   $Ph$   $Me$ 

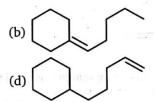
(c) 
$$\frac{Ph}{Me}C = C \frac{H}{Ph}$$

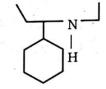
$$(d) \underset{Ph}{\text{Me}} C = C \underset{OE}{\underbrace{\text{Me}}}$$

46. 
$$\xrightarrow{LDA} A + N_2 + Ph - CH = CH_2, Product A is:$$

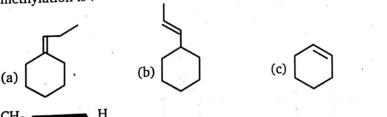
$$NH - CH_2 - CH_2 - Ph$$

LDA = Lithium di-isopropyl amide

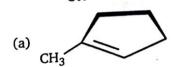


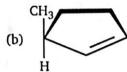


Major product of the reaction, when the given compound undergoes Hoffmann exhaustive methylation is :



48.  $H \xrightarrow{\text{POCl}_3} \text{Major product of the reaction is :}$ 





(d)  $H_2C = CH_2$ 

Stereochemistry of the product is:

- (a) Meso compound
- (c) Diastereomer

- (b) Racemic mixture
- (d) Optically pure enantiomers

Which of the following reactant is used to obtain above compound (A). (Assume that EtO<sup>-</sup> is used in all the reaction)

**51.** (A), Product A is:

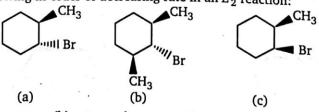


(b) C



(d)

**52.** Rank the following in order of decreasing rate in an  $E_2$  reaction:



(a) a > b > c

(b) c > a > b

(c) c > b > a

(d) b > a > c

53. Ph 
$$\xrightarrow{\text{KOH}} (A)$$
, Product  $(A)$  is :

54. 
$$\xrightarrow{\text{EtO}^{\ominus}} (A) \text{ Major}$$

$$\underbrace{NMe_3}_{\text{M}} \xrightarrow{\text{EtO}^{\Theta}} (B) \text{ Major}$$

Relation between (A) and (B) is:

(a) G.I.

- (b) Positional isomer
- (c) Enantiomer

(d) Chain isomer

55. Cl 
$$\xrightarrow{3\text{NaNH}_2}$$
 Product; The Product is:

(b) HC 
$$\equiv$$
 C  $-$  (CH<sub>2</sub>)<sub>3</sub>ONa

(c) NaC 
$$\equiv$$
 C  $-$  (CH<sub>2</sub>)<sub>3</sub>ONa

(d) 
$$H - C \equiv C - (CH_2)_3 OH$$

Which best describes the product of the following reaction? 56.

$$Ph \xrightarrow{CH_3} \xrightarrow{K^+t-BuO^-} product$$
Br

- (a) Absolute configuration has been inverted
- (b) Absolute configuration has been retained
- (c) Racemization (loss of absolute configuration) has occurred
- (d) Loss of chirality has occurred (the product is achiral)
- What is the major product of the following reaction? 57.

product of the following reaction?

OH

CH<sub>3</sub>

$$CH_3 - CH_2 - C - CH$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

(a) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

(b) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

(c) 
$$H$$
  $C = C$   $CH_2CH_3$ 

(d) 
$$CH_3$$
  $C = C$   $CH_3$   $CH_3$ 

- **58.** What will be the major product of each of the two reaction shown below?
  - 1.  $CH_3CH_2CHCH_3 \xrightarrow{heat}$   $+N(CH_3)_3-OH$ 2.  $CH_3CH_2CHCH_3 + CH_3CH_2ONa \xrightarrow{heat}$  X Y
  - Br (a) 1-X, 2-X

NHCH2CH3

- (b) 1 Y, 2 X
- (c) 1 X, 2 Y
- (d) 1 Y, 2 Y

59.

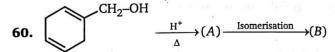
+  $CH_3I$  (excess)  $\longrightarrow$  product; The product is :

(a) a primary amine

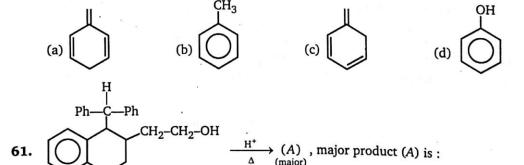
(b) a tertiary amine

(c) a secondary amine

(d) a quaternary ammonium salt



(A) on heating isomerizes to (B). What is the structure of (B)?



#### ALKYL HALIDES (ELIMINATION)

313

(a) 
$$CH_2-CH_3$$

$$(b) \begin{picture}(b){\columnwidth} \begin{picture}(b){\columnw$$

$$\begin{array}{c} \text{Ph} \\ \text{Ph-CH-OH} \\ \text{(d)} \end{array}$$

**62.** Which of the following carbocation will undergo rearrangement?

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

(d) 
$$CH_3 - NH - \overset{\oplus}{CH} - CH - CH_3$$
  
 $CH_3$ 

63. In which of the following reaction resonance stabilized product will form?

(a) 
$$CH_2$$
-OH  $H^+$   $\Delta$ 

(b) 
$$OH \xrightarrow{H^+ \Delta}$$

(c) 
$$OH \xrightarrow{H^+}$$

(d) All of these

64. In which of following reaction rearrangement take place with change in carbon skeleton?

(a) 
$$CH_3 - CH_2$$
  $CH_3 - CH_2$   $CH_3$ 

(b) 
$$CH_3 - CH_2CH_2^{\oplus}$$

(c) 
$$CH_3 - CH - CH_2 - \overset{\oplus}{CH_2}$$
  
 $CH_3$ 

(d) 
$$CH_3 - CH^{\oplus} - CH_3$$

65. Consider the following reaction:

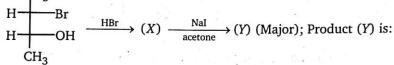
Which response contains all the correct statement about this process?

(1) Dehydration

- (2) E<sub>2</sub> mechanism
- (3) Carbon skeleton migration
- (4) Most stable alkene will form

- (5) Single-step reaction
- (a) 1, 3  $CH_3$
- (b) 1, 2, 3
- (c) 1, 2, 5
- (d) 1, 3, 4

66.



(a) cis-2-butene

(b) trans-2-butene

(c) 1-butene

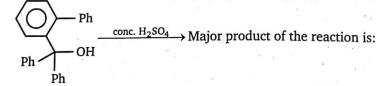
(d) Iso-butene

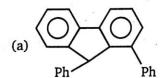
67. 
$$CH_2-CH=CH-CH_2$$
  $\xrightarrow{Zn (dust)}$   $(A)$ 

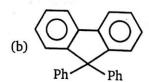
Above reaction is an example of 1,4-elimination. Predict the product.

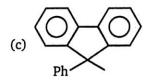
- (a)  $CH_3 CH = C = CH_2$ (c)  $CH_3 CH_2 C \equiv CH$
- (b)  $CH_3 C \equiv C CH_3$
- (d)  $H_2C = CH CH = CH_2$

68.









(d) None of these

Ph CH<sub>3</sub> Ph Et

| | | | | |

69. Ph 
$$-C - C - CH_3 + Ph - C - C - Et \xrightarrow{H_2SO_4}$$

OH OH OH OH OH

(A) (B)

$$\begin{array}{c|c} & \text{Ph} & \text{O} \\ & | & || \\ \text{(p)} & \text{Ph} - \text{C} - \text{C} - \text{CH}_3 \\ & | \\ & \text{CH}_3 \end{array}$$

$$\begin{array}{c|c} & \text{Ph} & \text{O} \\ & | & || \\ \text{(r)} & \text{Ph} - \text{C} - \text{C} - \text{CH}_3 \\ & | \\ & \text{Et} \end{array}$$

When (A) and (B) reacts with H<sub>2</sub>SO<sub>4</sub> products obtained are:

- (a) p, q, r, s
- (b) p, q
- (c) p, q, r
- (d) p, q, s
- **70.** Which of the following compound gives even number of Hoffmann's exhaustive methylation and elimination?





71.  $CH_3$  I  $CH_2$   $CH_3$   $CH_3$   $CH_4$   $CH_3$   $CH_3$   $CH_4$   $CH_3$   $CH_4$   $CH_3$  (including stereoisomer).

- (a) 2
- (b) 4

CH<sub>3</sub>

- (c) 6
- (d) 8

72. Cl  $\xrightarrow{t\text{-butO}^{\Theta}} (A)$ ; "(A)" is

(a) 
$$(b) \bigcup_{O} O^{\Theta}$$
(b) 
$$(c) \bigcup_{O} Cl \bigcup_{O} O t\text{-but}$$

73. 
$$\begin{array}{c} \text{Conc. H}_2\text{SO}_4 \rightarrow A + \text{H}_2\text{O} \\ \text{(Major)} \end{array}$$

which of the following is product "A" in the above reaction?

						ANSV	VERS	— LE	VEL 1						
1.	(d)	2.	A – a B– d	3.	(a)	4.	(c)	5.	(b)	6.	(b)	7.	(d)	8.	(b)
9.	(c)	10.	(d)	11.	(c)	12.	(c)	13.	(c)	14.	(d)	15.	(d)	16.	(c)
17.	(b)	18.	(b)	19.	(c)	20.	(a)	21.	(b)	22.	(a)	23.	(b)	24.	(a)
25.	(b)	26.	(a)	27.	(d)	28.	(c)	29.	(b)	30.	(c)	31.	(d)	32.	(d)
33.	(a)	34.	(a)	35.	(a)	36.	(b)	37.	(c)	38.	(c)	39.	(c)	40.	(c)
41.	(c)	42.	(b)	43.	(b)	44.	(b)	45.	(c)	46.	(a)	47.	(d)	48.	(b)
49.	(b)	50.	(a)	51.	(c)	52.	(b)	53.	(b)	54.	(b)	55.	(c)	56.	(d)
57.	(d)	58.	(b)	59.	(d)	60.	(b)	61.	(a)	62.	(b)	63.	(d)	64.	(a)
65.	(d)	66.	(b)	67.	(d)	68.	(b)	69.	(b)	70.	(a,b)	71.	(b)	72.	(b)
73.	(a)														



#### 1. Comprehension

 $E_2$  reaction  $\rightarrow$  Elimination bimolecular

In the general mechanism of the  $E_2$  reaction a strong base abstract a proton on a carbon atom adjacent to the one of the leaving group. As the base abstracts a proton, a double bond forms and the leaving group leaves.

$$CH_3 - CH_2 - CH - CH_3 \xrightarrow{CH_3ONa} \xrightarrow{CH_3OH} CH_3 \xrightarrow{(major)} H$$

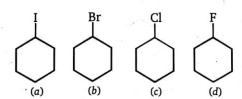
#### Mechanism:

$$CH_3ONa + CH_3 - CH - CH - CH_3 \longrightarrow \begin{bmatrix} CH_3O - - - H \\ CH_3 - CH - CH \end{bmatrix} + CH_3OH - CH$$

anti-coplanar transition state (staggered conformation -lower energy)



**A.** Identify the rate of reaction of given compounds in  $E_2$  reaction:



(a) a > b > c > d (b) a > c > b > d (c) b > a > c > d (d) b > d > a > c

**B.** In given pairs, which compound is more reactive toward  $E_2$  reaction:

$$(P) \qquad CH_3 \qquad CH_3 \qquad (II) \qquad (III) \qquad CH_3 - CH - CD_3 \qquad Br \qquad (III) \qquad Br \qquad (IV)$$

$$\begin{array}{c}
 & \text{Br} \\
 & \text{(VI)} \\
 & \text{Ph} - \text{CH} - \text{CH}_{3} \\
 & \text{Br} \quad \text{(VIII)}
\end{array}$$

(b) 
$$P - II$$
,  $Q - III$ ,  $R - VI$ ,  $S - VI$ 

(d) 
$$P-I$$
,  $Q-II$ ,  $R-V$ ,  $S-VIII$ 

C. 
$$CH_3 \xrightarrow{Ph} H$$
 $CH_3 \xrightarrow{Br} Br$ 
 $Alc.KOH \rightarrow (A)$ 

Ph

Product (A) and (B) are: (a) A = cis, B = cis

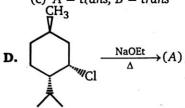
(c) 
$$A = trans$$
,  $B = trans$ 

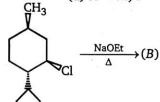
$$\begin{array}{c|c}
Ph \\
CH_3 & H \\
Br & CH_3
\end{array}$$

$$\xrightarrow{Alc.KOH} (B)$$

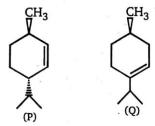
(b) A = trans, B = cis

(d) 
$$A = cis$$
,  $B = trans$ 





Select the products (A) and (B) from the compounds (P) and (Q) given below:



(a) 
$$A = P$$
,  $B = P$ 

(b) 
$$A = Q$$
,  $B = Q$  (c)  $A = Q$ ,  $B = P$ 

(d) A = P, B = Q

**E.** Which of the following compound is inert toward  $E_2$  reaction.

(d) 
$$CH_3 - C - CH - CH_3$$
  
 $CH_3 Br$ 

	Column (I)	Column (II)				
	$E_2$ reaction (elimination bimolecular)	No. of possible products. (including stereoisomerism)				
(a)	$ \begin{array}{c} \text{Br} \\ \text{alc. KOH} \\ \Delta \end{array} $	(p)	0			
(ь)	$\xrightarrow{\text{alc. KOH}} \Delta$	(q)	1			
(c)	$Br \xrightarrow{\text{alc. KOH}} \Delta$	(r)	2			
(d)	$Br \xrightarrow{\text{alc. KOH}} \Delta$	(s)	3			

#### 3. Match the Column:

HEM = Hoffmann exhaustive methylation followed by elimination.

	Column (I)		Column (II)	
	Reaction	Product		
(a)	HEM HEM	(p)	$H_2C = CH - CH_2 - CH = CH_2$	
(b)	$ \begin{array}{c}                                     $	(q)	$H_2C = CH - CH_2 - CH_2 - CH = CH_2$	
(c)	HEM HEM	<b>(r)</b>	$\begin{array}{c} \text{CH}_3 \\ \text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{C} = \text{CH}_2 \end{array}$	
(d)	HEM HEM	(s)	$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{H}_2\text{C} = \text{CH} - \text{CH} - \text{CH} = \text{CH}_2 \end{array}$	

	Column (I)	Column (II)		
(a)	$OH \xrightarrow{H^{\oplus}}$	(p)	Product are Diastereomers	
(b)	$ \begin{array}{c}  & \text{alc. KOH} \\  & \Delta \end{array} $	(q)	Carbocation is intermediate	
(c)	$OH \xrightarrow{H^{\oplus}}$	(r)	2nd order reaction	
(d)	$ \underbrace{Br}^{alc. KOH} \xrightarrow{\Delta} $	(s)	Ist order reaction	

#### 5. Match the column :

	Column (I)	Column (II)		
(a)	Cl alc. KOH	(p)	Optically active product	
(b)	Cl alc. KOH	(q)	Optically inactive product	
(c)	Cl aq. KOH	(r)	2nd order reaction	
(d)	$ \begin{array}{c} Cl \\                                   $	(s)	unimolecular reaction	

	Column (I)	Column (II)			
	E <sub>2</sub> reactions (elimination bimolecular)	Number of products (including stereoisomerism)			
(a)	$CH_3 - CH_2 - CH_2 - CH_2 - Br \xrightarrow{alc. KOH}$	(p)	1		
(ь)	$CH_3-CH-CH_2-CH_3 \xrightarrow{alc. KOH} $ $\downarrow$ $Br$	(q)	2		
(c)	$CH_{3}$ $CH_{3} - C - CH_{2} - CH_{3} \xrightarrow{alc. KOH}$ $Br$	(r)	3		
(d)	Ph -CH <sub>2</sub> -CH-CH <sub>2</sub> -CH <sub>3</sub>   Br	(s)	4		

#### 7. Match the column:

	Column (I)	Column (II)		
(a)	$ \begin{array}{c}  & H^{+} \\ \hline OH & \Delta \end{array} $ (A)	(p)	$E_1$	
(ь)	$ \begin{array}{c}                                     $	(q)	E <sub>2</sub>	
(c)	$CH_3 - C - CH_2 - CH - CH_3 \xrightarrow{EtONa} \Delta$ Br	(r)	Ei (elimination intramolecular)	
(d)	$\bigcup_{\substack{\Phi \\ N \\ Me}} Me \xrightarrow{\Delta}$	(s)	E <sub>1CB</sub>	

		ATTENDED OF	
A SERVE	Column (I)		Column (II)
	Reaction	19 1 N	Product
(a)	$\bigcap_{D} \bigoplus_{Me}^{Me} \bigcap_{\Delta}$	(p)	D
(b)	$\bigcap_{\mathbf{M} \in \mathcal{N}} \bigcap_{\mathbf{M} \in $	(q)	H
(c)	$ \begin{array}{c} \stackrel{\oplus}{\longrightarrow} Me \\ \stackrel{Me}{\longrightarrow} Me \\ \stackrel{\ominus}{\longrightarrow} Me \\ \stackrel{\longleftarrow}{\longrightarrow} Me $	(r)	$CH_3$
(d)	$\begin{array}{c} O^{\Theta} \\ Me \\ Me \\ CD_{3} \end{array}$	(s)	$\bigcirc \bigcirc $

# 9. (a) $\xrightarrow{\text{alc. KOH}}$ (X) products (b) $\xrightarrow{\text{Br}}$ $\xrightarrow{\text{alc. KOH}}$ (Y) (c) $\xrightarrow{\text{Br}}$ $\xrightarrow{\text{alc. KOH}}$ (Z) (d) $\text{CH}_3$ $\xrightarrow{\text{CH}_3}$ $\xrightarrow{\text{H}}$ $\xrightarrow{\text{alc. KOH}}$ (P)

Sum of X + Y + Z + P =

Reaction-1: 
$$Ph - C - CH_3$$
  $\xrightarrow{PCl_5}$   $\xrightarrow{x NaNH_2}$   $\xrightarrow{CH_3I}$   $Ph - C \equiv C - CH_3$ 

Reaction-2:  $\xrightarrow{y NaNH_2}$   $CH_3 - C \equiv C - CH_3$ 

Reaction-3:  $Ph - CH - CH_2$   $\xrightarrow{z NaNH_2}$   $\xrightarrow{Et - I}$   $Ph - C \equiv C - Et$   $Cl$   $Cl$ 

x, y, z are moles used.

Sum of [x+y+z=]

11. Sum of  $\alpha$ -hydrogen in major product of the reaction.

Reaction-1

Reaction-2

$$H^+ \rightarrow (A)$$
 $OH$ 
 $H^+ \rightarrow (B)$ 
 $OH$ 

Reaction-3

 $H^+ \rightarrow (C)$ 
 $OH$ 
 $O$ 

Sum of  $\alpha$ -hydrogen is A + B + C + D =

12. Reaction-1 
$$CH_3 - C - CH - CH_3 \xrightarrow{H^+} \Delta (A)$$

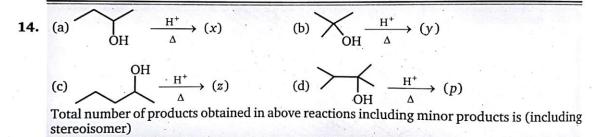
Reaction-2  $CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{H^+} \Delta (B)$ 

$$CH_3 \xrightarrow{CH_3} CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{CH_3} CH_3 - CH_2 - CH_3 \xrightarrow{CH_3} CH_3 - CH_3 \xrightarrow{CH_3} CH_3 - CH_3 \xrightarrow{CH_3} CH_3 - CH_3 \xrightarrow{CH_3} CH_3 - CH_3 - CH_3 \xrightarrow{CH_3} CH_3 - C$$

Sum of  $\alpha$ -hydrogen is (A + B + C = )

13. Reaction-1 
$$H^+ \to (A)$$
Reaction-2  $H^+ \to (B)$ 
 $(B)$ 
 $(M) \to (B)$ 
 $(M) \to (M)$ 
 $(M) \to (M$ 

Sum of  $\alpha$ -hydrogen (A + B + C) =



#### 15. Match the column (I) and (II).

	Column (I)		Column (II)
	Reaction		Type of Reaction
(a)	R -2 -chlorobutane $\xrightarrow{\text{KSH}}$	(p)	$S_{N^1}$
(b)	R - 2- chlorobutane $\xrightarrow{\text{EtO}^-\text{Na}}$ EtOH	(q)	$S_{N^2}$
(c)	2 - bromo- 2- methyl propane $\longrightarrow$ H <sub>2</sub> O	(r)	$E_1$
(d)	2- butanol $\xrightarrow{\text{H}_2\text{SO}_4}$ $\xrightarrow{\Delta}$	(s)	E <sub>2</sub>

#### 16. Match the column (I) and (II).

	Column (I)		Column (II)
	Reaction		Type of Reaction
(a)	Cl aq.KOH →	(p)	$S_{N^1}$
(b)	Cl alc.KOH →	(q)	<i>S</i> <sub>N</sub> <sup>2</sup>
(c)	$ \begin{array}{c}  & \\  & \\  & \\  & \\ \end{array} $ Cl $ \begin{array}{c}  & \\  & \\  & \\ \end{array} $	(r)	$E_1$
(d)	$ \begin{array}{c}  & \xrightarrow{H^+} \\  & \xrightarrow{\Delta} \end{array} $	(s)	E <sub>2</sub>

17. Select whether the following reagent combination will result in elimination or substitution reactions leading to the major product.

	Reaction	Substitution	Elimination
(a)	$CH_{3}$ $CH_{3} \longrightarrow C \longrightarrow Cl \xrightarrow{K^{\oplus} \ OC(CH_{3})_{3}} \longrightarrow H_{2}O$ $H$		
(b)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 -   \\ \text{C} -   \\ \text{OH} \xrightarrow{\text{H}_2 \text{SO}_4} \\   \\ \text{CH}_3 \end{array}$		

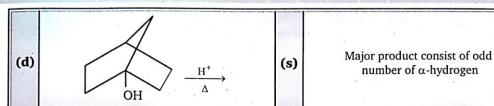
(c)	$\begin{array}{c} \text{Cl} \\ \mid \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 & \xrightarrow{\text{alc-KOH}} \end{array} \rightarrow$		
(d)	$ \begin{array}{c} CH_{3} \\  \downarrow \\ CH_{3} - C - I \xrightarrow{\text{Na N}_{3}} \\  \downarrow \\  H \end{array} $		
(e)	$Cl_{3} \xrightarrow{EtO^{-}} \Delta$	*	2
<b>(f)</b>	$ \begin{array}{c} CH_3 \\   \\ CH_3 - C - Cl \xrightarrow{H_2O} \\   \\ CH_3 \end{array} $		

18. Match the Column (I) and (II) (Matrix).

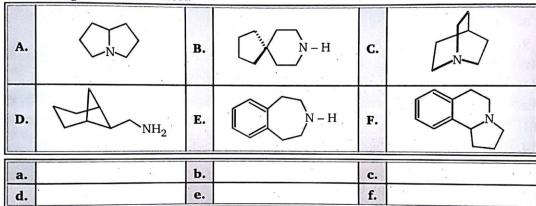
	Column (I)		Column (II)
	Reaction		Comment on product
(a)	$ \begin{array}{c} CH_3 \\ & \xrightarrow{H^+} \\ OH \end{array} $	(p)	Racemic mixture
(b)	$ \begin{array}{c}                                     $	(q)	Major product consist of even number of $\alpha$ -hydrogen
(c)	$\stackrel{\text{OH}}{\longrightarrow} \stackrel{\text{H}^+}{\longrightarrow}$	(r)	Will not undergo dehydration

#### ALKYL HALIDES (ELIMINATION)

327



19. For each of the following amines (A through D), exhaustive methylation (treatment with excess methyl iodide), followed by Hoffmann elimination (heating with AgOH), repeated as necessary, removes the nitrogen atom in the form of trimethylamine. Indicate the number of repetitive Hoffmann eliminations required to remove the nitrogen by a number (1 to 4) in the designated answer sheet.



20.

$$x$$
 is total number of HEM (Hoffman Exhaustive Methylation and eliminations) to remove nitrogen from given compound.

 $x$  is total number of possible  $x$  product (including stereoisomer)

Sum of x+y=?

21.

$$\begin{array}{c|c} CH_3 \\ CH_3-CH-CH-CH_3 \\ Br & \xrightarrow{EtOH} (x) & (S_{N^1}+E_1) & \text{products. (including stereoisomer)} \\ & \text{consider all products} \end{array}$$

Total number of products are:

#### ANSWERS — LEVEL 2

1. 
$$A-a$$
;  $B-a$ ;  $C-b$ ;  $D-c$ ;  $E-c$ ;

2. 
$$a-s$$
;  $b-r$ ;  $c-q$ ;  $d-p$ 

3. 
$$a-s$$
;  $b-r$ ;  $c-q$ ;  $d-p$ 

4. 
$$a-p, q, s; b-p, r; c-q, s; d-r$$

5. 
$$a - p, r; b - p, r; c - p, r; d - q, r$$

6. 
$$a-p; b-r; c-q; d-s$$

7. 
$$a-p$$
;  $b-q$ ;  $c-s$ ;  $d-r$ 

8. 
$$a-p; b-q; c-r; d-s$$

**9.** 
$$X = 3$$
,  $Y = 3$ ,  $Z = 2$ ,  $P = 0 \Rightarrow 3 + 3 + 2 + 0 = 8$ 

**10.** 
$$x = 3$$
,  $y = 2$ ,  $z = 3 \Rightarrow 3 + 2 + 3 = 8$ 

**14.** 
$$x = 3$$
,  $y = 1$ ,  $z = 3$ ,  $p = 2$   
Sum = 9

**15.** 
$$(a-q)$$
,  $(b-s)$ ,  $(c-p)$ ,  $(d-r)$ 

**16.** 
$$(a-q)$$
,  $(b-s)$ ,  $(c-p)$ ,  $(d-r)$ 

**18.** 
$$a-p, q; b-p, q; c-q; d-r$$

**19.** 
$$a-3$$
;  $b-2$ ;  $c-3$ ;  $d-1$ ;  $e-2$ ;  $f-3$ 

## 5c

### **ALKYL HALIDES**



# LEVEL- Z

1. One eq. NaCN
$$\frac{1. \text{ One eq. NaCN}}{2 \text{ LiAlH}_4} (A); \text{ Product } (A) \text{ is :}$$

(c) 
$$Br$$
  $CH_2NH_2$ 

2. In the reactions given below,

$$R - Cl \xrightarrow{\text{(i) KCN, (ii) LiAlH}_4} \text{Product } A$$

$$R - Cl \xrightarrow{\text{(i) AgCN, (ii) LiAlH}_4} \text{Product } B$$

the compounds A and B are:

(a) chain isomers

(b) position isomers

(c) functional isomers

(d) metamers

**3.** Which is the major product expected from the following  $S_{N^2}$  reaction?

**4.** Consider the following  $E_1/S_{N^1}$  reaction:

- (a) 1, 2 and 3 (b) 3 and 4
- (2) H CH<sub>3</sub>
- (4) H<sub>3</sub>C H
- (c) 2 and 3
- (d) 1, 2, 3 and 4

ALKYL HALIDES 331

**5.** What is the product of the following  $S_{N^2}$  reaction?

OTS O NaBr Product

OMe 
$$S_{N^2}$$
 Product

OMe  $S_{N^2}$  OMe

- **6.** Select the reagent that will yield the greater amount of substitution on reaction with  $CH_3 CH_2 Br$ :
  - (a) CH<sub>3</sub>CH<sub>2</sub>OK in dimethyl sulfoxide (DMSO)
  - (b) (CH<sub>3</sub>)<sub>3</sub>COK in dimethyl sulfoxide (DMSO)
  - (c) Both (a) and (b) will give comparable amounts of substitution
  - (d) Neither (a) nor (b) will give any amount of substitution
- 7. Under the specified conditions, substrate X undergoes substitution and elimination reactions to give products A D. A and B are stereoisomers, but not enantiomers. C and D are enantiomers. A is not an isomer of C. Which of the following could be the starting material X?

Compare rate of E2 reaction:

(a) 
$$c > b > a$$
 (b)  $a > b > c$  (c)  $b > a > c$  (d)  $c > a > b$ 

9. Which reaction results in the formation of a pair of enantiomers?

**10.** Rate limiting  $S_{N^1}$  follows the sequence

$$\stackrel{\delta \oplus}{R-} \stackrel{\delta \ominus}{R-} \stackrel{R^{\oplus}}{\longleftarrow} \stackrel{Br^{\ominus}}{\longleftarrow} \stackrel{R^{\oplus}}{\longleftarrow} \stackrel{Br^{\ominus}}{\longleftarrow} \stackrel{Br^{\ominus}}{\longrightarrow} \stackrel{Br^{\ominus}}$$

True statement about sequence on the basis of assumption that R contains 3 different groups is :

- (a) more stable carbocation, greater is in the proportion of racemization
- (b) the more nucleophilic the solvent greater in the proportion of inversion
- (c) In above sequence (b) represent separately solvated, pair of ions
- (d) All of these
- 11. Compare the two methods shown for the preparation of carboxylic acids :

Method 1: 
$$RBr \xrightarrow{Mg} RMgBr \xrightarrow{1. CO_2} RCO_2H$$

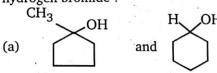
Method 2:  $RBr \xrightarrow{NaCN} RCN \xrightarrow{H_2O, HCl} RCO_2H$ 

Which one of the following statements correctly describes this conversion?

$$\bigoplus_{Br} \longrightarrow \bigoplus_{CO_2H}$$

- (a) Both method 1 and method 2 are appropriate for carrying out this conversion
- (b) Neither method 1 nor method 2 is appropriate for carrying out this conversion
- (c) Method 1 will work well, but method 2 is not appropriate
- (d) Method 2 will work well, but method 1 is not appropriate
- 12. Which of the following statements is true?
  - (a) CH<sub>3</sub>CH<sub>2</sub>S<sup>-</sup> is both a stronger base and more nucleophilic than CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>
  - (b) CH<sub>3</sub>CH<sub>2</sub>S<sup>-</sup> is a stronger base but is less nucleophilic than CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>
  - (c) CH<sub>3</sub>CH<sub>2</sub>S<sup>-</sup> is a weaker base but is more nucleophilic than CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>
  - (d) CH<sub>3</sub>CH<sub>2</sub>S<sup>-</sup> is both a weaker base and less nucleophilic than CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>

**13.** In the given pair of alcohols, in which pair second alcohol is more reactive than first towards hydrogen bromide?



(c) 
$$\mathrm{CH_3}$$
 –  $\mathrm{CH}$  –  $\mathrm{CH_2}$  –  $\mathrm{CH_3}$  and  $\mathrm{CH_3}$  –  $\mathrm{CH_2}$  –  $\mathrm{CH}$  –  $\mathrm{CH_2}$  –  $\mathrm{OH}$  OH

(d) 
$$CH_3 - CH - CH_2 - CH_3$$
 and  $(CH_3)_2C - CH_2 - CH_3$  OH

14. Which product would be expected to predominate in the given reaction?

$$(a) \bigcirc OSO_2CF_3$$

$$CH_3OH \longrightarrow \Delta(30^\circ C)$$

$$O-SO_2-CH_3$$

$$(b) \bigcirc O$$

$$O-SO_2-CH_3$$

$$(c) \bigcirc O$$

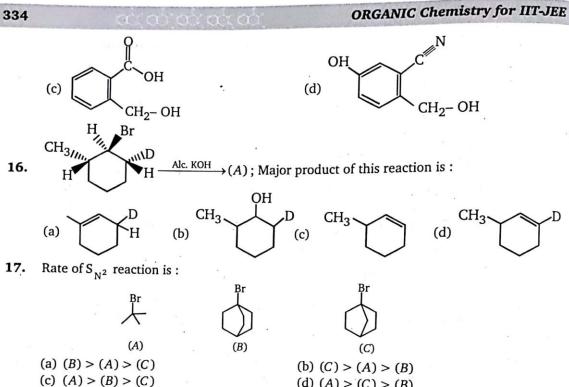
$$O-SO_2-CH_3$$

$$O-SO_2-CH_3$$

$$O-SO_2-CH_3$$

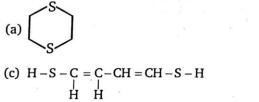
**15.** Which is the major product of the following reaction?

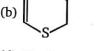
(a) 
$$CH_{2}$$
- Br



(d) (A) > (C) > (B)1-2-dichloro ethane + NaSCH<sub>2</sub>CH<sub>2</sub>SNa $\longrightarrow$  C<sub>4</sub>H<sub>8</sub>S<sub>2</sub> + (P) 18.

Unknown product (P) of the above reaction is:



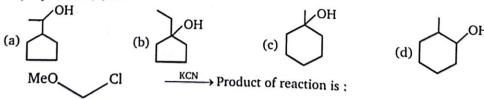


(d) 
$$H - C = C - CH = CH - S - H$$
  
 $H \quad H$ 

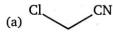
19. 
$$\xrightarrow{\text{Moist Ag}_2O}$$
 (A) product

Major product (A) is:

20.



(MOM chloride) (Methoxy methyl chloride)

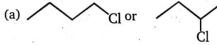


(b) MeO CN

(c)  $Me - O - CH_2 - CH_2 - CN$ 

(d) O < CN

21. In the given pair of compound, in which pair the second compound is more reactive than first toward  $S_{N^2}$  reaction?



(b)  $CH_2 - Cl$  or Cl

(c) 
$$\xrightarrow{Br}$$
 or  $\xrightarrow{Br}$ 

 $(d) \qquad \bigvee_{Cl} \qquad or \qquad \bigvee_{Cl} \qquad (d)$ 

**22.** Which compound might be synthesized by the  $S_{N^2}$  displacement of an alkyl-halide?

(b) SCH<sub>2</sub>CH<sub>3</sub>

(c)  $Me_3C - OCH_3$ 

(d) All of these

**23.** Identify C in the following series  $C_3H_7I \xrightarrow{KOH} A \xrightarrow{NBS} B \xrightarrow{KCN} C$ .

(a) 
$$(CH_3)_2CH-CN$$

(b) 
$$CH_2 = CH - CH_2CN$$

(c) 
$$Br - CH = CH - CN$$

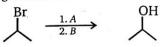
(d) 
$$CH_2 = CH - CHCN$$

24. What sequence of reagents is required to accomplish the following transformation?



- (a) (1) NBS, ROOR (2)  $CH_3CH_2O^-$  (3) 2HBr (4)  $NH_2^-$  (5) disiamyl borane (6)  $H_2O_2$ ,  $OH^-$
- (b) (1)  $\mathrm{Cl_2}\,\mathrm{hv}$  (2)  $\mathrm{OH^-}$ , heat; (3) 2HCl (4)  $\mathrm{OH^-}$ , heat (5)  $\mathrm{HgSO_4}$ ,  $\mathrm{H_2SO_4}$
- (c) (1) NBS, ROOR; OH-, DMSO
- (d) (1) Br<sub>2</sub>, hv (2) t-butoxide (3) BH<sub>3</sub>, THF (4) H<sub>2</sub>O<sub>2</sub>, OH<sup>-</sup>

25. Which of the reagents shown below would accomplish the following transformations?



A

E

(a)  $H_3O^+$ 

BH<sub>3</sub> -THF; H<sub>2</sub>O<sub>2</sub>/NaOH

(b) NaOH

BH<sub>3</sub> -THF; H<sub>2</sub>O<sub>2</sub>/NaOH

(c) HBr in ether

Hg(OAc)<sub>2</sub>/H<sub>2</sub>O; NaBH<sub>4</sub>

(d) NaNH<sub>2</sub>

Hg(OAc)<sub>2</sub>/H<sub>2</sub>O; NaBH<sub>4</sub>

26. What are the products obtained from the following reaction?

$$\begin{array}{c}
\text{Br} \\
\xrightarrow{\text{HC} = \text{CNa}} \\
\xrightarrow{\text{Et}_2\text{O}}
\end{array}$$
 Product

(a) 
$$C^{C}$$
 +  $C^{C}$  (b)  $C^{C}$  +  $C^{C}$  +  $C^{C}$  (c)  $C^{C}$  (d)  $C^{C}$  100%

**27.** The back-side attack on 2-bromobutane by methoxide (CH<sub>3</sub>O<sup>-</sup>) gives the product shown below. Which Fischer projection represents 2-bromobutane used as the reactant in this reaction?

- 28. Consider the following statements:
  - (1) Bridgehead halides are inert towards both  $S_{N^1}$  and  $S_{N^2}$  reactions (till one of the ring size is eight member ring)
  - (2) The first step in both  $S_{N^1}$  and  $E_1$  reactions is the same
  - (3)  $S_{N^2}$  reactions proceed with total retention of configuration
  - (4) E<sub>2</sub> eliminations are by the use of a solvent of low polarity and high concentration of a strong base

Which of the above statements are correct?

(a) 1, 2 and 4

(b) 1 and 3

(c) 2, 3 and 4

- (d) 1, 2, 3 and 4
- 29. Consider the following alcohols:

$$\bigcirc \stackrel{CH_2OH}{\bigodot} \bigcirc \stackrel{CH_2OH}{\bigcirc} \bigcirc \stackrel$$

The order of decreasing reactivities of these alcohols towards substitution with HBr is:

(a) III > I > IV > II

VI < II < I < II (d)

(c) I > III > IV > II

VI < II < III < I (b)

- In solvolysis of 1,2-dimethyl propyl p-toluene sulfonate in acetic acid at 75°C, how many (alkene + substitution) products will be formed?
- (b) 3 ·
- (d) 5
- Benzotrichloride reacts with milk of lime to form: 31.
  - (a) Benzal
- (b) Benzoic acid
  - (c) Benzyl alcohol
- (d) Phenol
- $Br CH_2 (CH_2)_2 CH_2 Br + CH_3NH_2 \longrightarrow Product of the reaction is :$

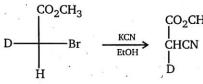








The configurations of the reactant and the product in the following reaction, respectively, 33.



- (a) R, R
- (b) R, S
- (d) S, S
- 1-4-dichlorohexane (1 mole) + NaI (1 mole) Acetone Product of the reaction is :

  - (a)  $Cl CH_2 CH_2 CH_2 CH_3 CH_2 CH_3 CH_2 CH_2 CH_2 CH_3 CH_3$

  - (c)  $H_2C = CH CH_2 CH_3$  (d)  $I CH_2 CH_2 CH_2 CH_2 CH_3$
- Alkyl halides can be obtained by all methods except: 35.
  - (a)  $CH_3CH_2OH + HCl/ZnCl_2 \longrightarrow$
- (b)  $CH_3 CH_2 CH_3 CH_2 \xrightarrow{Cl_2/UV \text{ light}}$
- (c)  $C_2H_5OH + NaCl \longrightarrow$
- (d)  $CH_3COOAg + Br_2/CCl_4 \longrightarrow$
- In order to prepare 1-chloropropane, which of the following reactants can be employed? 36.
  - (a) Propene and HCl in the presence of peroxide
  - (b) Propene and Cl<sub>2</sub> followed by treatment with aq. KOH
  - (c) Propanol-1 and SOCl<sub>2</sub>/pyridine
  - (d) Any of the above can be used
- Which alkyl halide has maximum density? 37.
  - (a) C<sub>3</sub>H<sub>7</sub>I
- (b)  $C_2H_5I$
- (c) CH<sub>3</sub>I
- (d) CH<sub>3</sub>Br
- Which of the following molecules would have a carbon-halogen bond most susceptible to 38. nucleophilic substitution?
  - (a) 2-fluorobutane

(b) 2-chlorobutane

(c) 2-bromobutane

(d) 2-iodobutane

- **39.** When benzyl chloride is treated with ethanolic KCN, the major product formed is :
  - (a) benzyl ethyl ether (b) benzyl alcohol
- (c) benzyl cyanide
  - (d) benzyl isocyanide
- **40.** Which of the following is most reactive towards nucleophilic substitution reaction?
  - (a)  $CH_2 = CH Cl$

(b)  $C_6H_5Cl$ 

(c)  $CH_3CH = CHCl$ 

- (d)  $ClCH_2 CH = CH_2$
- **41.** Which of the following reaction will not give ether as a major product?
  - (a)  $CH_3CH_2Cl + Ag_2O(dry) \longrightarrow$
- (b)  $(CH_3)_3CCl + CH_3CH_2O^-Na^+$

(c) 
$$CH_3CH_2Cl + Na^+O^-$$

(d) 
$$CH_3Cl + Na^+O^- - C - CH_3 \longrightarrow$$

42. 
$$0 - S - 0$$
  $C_{R_{2}}$  (A)

Product (A) and (B) in above reaction is:

(a) 
$$O^{-} = S = O = H, O^{-} = S = O = CH_{3}$$
 (b)  $O^{-} = S = O = H, O^{-} = S = CH_{3}$ 

(c) 
$$O^{-} = S = O - CH_{3}$$
,  $O = S = H$ 

$$(d) O^{-} - \overset{O}{\overset{\parallel}{=}} S - O, O^{-} - \overset{O}{\overset{\parallel}{=}} - O^{-}$$

ANSWERS — LEVEL 1															
1.	(c)	2.	(c)	3.	(b)	4.	(a)	5.	(a)	6.	(a)	7.	(c)	8.	(b)
9.	(b)	10.	(d)	11.	(c)	12.	(c)	13.	(d)	14.	(a)	15.	(c)	16.	(c)
17.	(c)	18.	(a)	19.	(c)	20.	(b)	21.	(d)	22.	(d)	23.	(b)	24.	(d)
25.	(d)	26.	(b)	27.	(d)	28.	(a)	29.	(a)	30.	(d)	31.	(b)	32.	(b)
33.	(d)	34.	(d)	35.	(c)	36.	(c)	37.	(a)	38.	(d)	39.	(c)	40.	(d)
41.	(b)	42.	(b)	TERRO		NEO-		Huma		alas est			(6)		



# LEVEL-2

**1.** The following organic halide derivatives (*A* to *J*) are reacted in ethanol solution with each of the nucleophiles: acetate, methylthiolate, cyanide and hydroxide anions. Six possible results from these combinations of reactants are designated (1) through (6) below:

Write the number corresponding to your best estimate of the outcome of each reaction in the appropriate answer box below.

Cl	CH <sub>2</sub> -Cl	CH <sub>3</sub> – I	$H_3C$ $H_3C$ $H$	CH <sub>3</sub>
A	В	С	D	Е
Br	cl	H H H	CH <sub>2</sub> – Br H <sub>3</sub> C	H <sub>3</sub> C
F	G	Н	I	J

#### **Possible Outcome:**

- (1) No reaction
- (3) Elimination
- (5) No reaction or slow substitution
- (2) Substitution
- (4) Substitution and elimination
- (6) No reaction or slow elimination

	Compound	A	В	С	D.	E	F	G	H	I	J
(i)	CH <sub>3</sub> CO <sub>2</sub> Na										
(ii)	CH <sub>3</sub> SNa						*				
(iii)	NaCN										
(iv)	NaOH										

2.	In each of the following sections three organic halogen compounds are listed. In the box
	given enter a number (1 to 3) indicating the order of reactivity of the designated (1 is most
	reactive and 3 is least).

(a) S <sub>N<sup>2</sup></sub> substitution by Na	OCOCH <sub>2</sub> in methanol:			
1. CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br □	2. (CH <sub>3</sub> ) <sub>2</sub> CHBr		3. $CH_2 = CHCH_2Br$	
(b) S <sub>N<sup>2</sup></sub> substitution by Na	I in acetone:			_
	2. C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl		3. C <sub>6</sub> H <sub>5</sub> CHClCH <sub>3</sub>	- 🔲
(c) S <sub>N<sup>2</sup></sub> substitution by N	aCN in methanol:			_
1. CH <sub>3</sub> CH <sub>2</sub> Cl	2. CH <sub>3</sub> CH <sub>2</sub> F	20	3. CH <sub>3</sub> CH <sub>2</sub> I	
(d) S <sub>N<sup>2</sup></sub> substitution by N	aSCH <sub>3</sub> in methanol:			_
1. (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub>	Br□ 2. CH <sub>3</sub> CH <sub>2</sub> CHB <sub>1</sub>	$CH_2CH_3\square$	3. $(CH_3)_3CCH_2Br$	

3. Isobutyl alcohol (2-methyl-1-propanol), (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH, can be transformed to each of the compounds (a through l) listed in the left-hand column. In each case the number of steps needed to accomplish the change is noted, and an answer box is provided for your reagent selections. Fourteen reagents (designated A through N) are listed in the right-hand column.

Write letters designating the reagent or reagents you believe will achieve the desired transformation in the box to the right of the product formula. In the case of a multi-step sequence write the reagents in the order they are to be used. In some cases you may wish to use a previously prepared compound as a reactant. If so, write the number (a to l) corresponding to the desired compound.

	Desired product		Write Options		Reagent List			
a.	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Br	one	8 1	A.	Hg(OAc) <sub>2</sub> in H <sub>2</sub> O			
ь.	$(CH_3)_2C = CH_2$	one	100 to	В.	PBr <sub>3</sub> & heat			
c.	$(CH_3)_2$ CHCH = O	one		C.	NaBH <sub>4</sub> in alcohol			
d.	(CH <sub>3</sub> ) <sub>2</sub> CHCO <sub>2</sub> H	one	2	D.	LiAlH <sub>4</sub> in THF (aqueous workup)			
e.	(CH <sub>3</sub> ) <sub>3</sub> CBr	two		E.	NaCN in alcohol			
f.	$(CH_3)_2CHCH_2C \equiv N$	two		F.	PCC in CH <sub>2</sub> Cl <sub>2</sub>			
g.	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OCOCH <sub>3</sub>	one		G.	Jones' reagent (CrO <sub>3</sub> in H <sub>3</sub> O <sup>+</sup> )			
h.	(CH <sub>3</sub> ) <sub>2</sub> CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	two	at the same of the	H.	HBr in CH <sub>2</sub> Cl <sub>2</sub>			
i.	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OCH <sub>2</sub> (CH <sub>3</sub> )	two		I.	H <sub>3</sub> PO <sub>4</sub> and heat			
j.	(CH <sub>3</sub> ) <sub>3</sub> COH	three		J.	(CH <sub>3</sub> CO) <sub>2</sub> O + pyridine			
k.	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> NH <sub>2</sub>	three		K.	NaN <sub>3</sub> in aqueous alcohol			
1.	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	two		L.	C <sub>6</sub> H <sub>5</sub> CO <sub>3</sub> H in CH <sub>2</sub> Cl <sub>2</sub> (peracid)			
				M.	NaH in ether and heat			
				N.	C <sub>2</sub> H <sub>5</sub> OH + acid catalyst & heat			

#### SUBJECTIVE PROBLEMS

1. 
$$CH_3$$
 $CH_3OH$ 
 $CH_3OH$ 
?

X=Total number of substitution and elimination product(s). Find the value of X.

ANSWERS — LEVEL 2											
Α	В	C	D	E	F	G	Н	I	J		
2	2	2	1 .	1	1	6	2	2	. 6		
2	2	2	1	1	5	6	2	2	6		
2	2	2	1	1	. 1	3	3	2	3		
4	. 2	2	1	1	5	3	3	4	3		
	2 2 2	2 2 2 2 2 2	A B C 2 2 2 2 2 2 2 2 2	A B C D 2 2 2 1 2 2 2 1 2 2 2 1	A B C D E 2 2 2 1 1 2 2 2 1 1 2 2 2 1 1	A B C D E F 2 2 2 1 1 1 2 2 2 1 1 5 2 2 2 1 1 1	A B C D E F G 2 2 2 1 1 1 6 2 2 2 1 1 5 6 2 2 2 1 1 1 3	A B C D E F G H 2 2 2 1 1 1 6 2 2 2 2 1 1 5 6 2 2 2 2 1 1 1 3 3	A B C D E F G H I 2 2 2 1 1 1 6 2 2 2 2 2 1 1 5 6 2 2 2 2 2 1 1 1 3 3 2		

- **2.** a-3>1>2; b-2>3>1; c-3>1>2; d-1>2>3
- 3. a-B; b-I; c-F; d-G; e-I, H or 2 H; f-B, E or 1, E; g-J; h-G, N or 4N i-N, j-I, A, C or 2AC or ILD or 2LD; k-B, K, D or 1KD; l-B, E, D or 1ED or 6D

#### **Subjective Problems**

**1.** 4

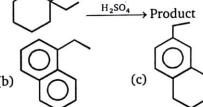
## **ALCOHOL, ETHERS AND EPOXIDES**

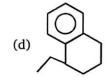


**1.** The following transformation involves a carbocation rearrangement. The carbocation is generated by protonation of the hydroxyl group, followed by the loss of water. Which bond has to migrate in the carbocation to yield the product indicated (after the deprotonation)?

$$(b) \xrightarrow{H_2SO_4} (c)$$

$$(a) \xrightarrow{(a)} (c)$$





$$CH_2 - O - C - CH_3$$

$$CH_2 - OH$$

$$CH_2 - OH$$

$$CH_2 - OH$$

$$CH_3$$

$$CH_2 - CH_3$$

$$CH_3$$

$$CH_4$$

$$CH_2 - CH_3$$

$$CH_4$$

$$CH_5$$

$$C - CH_3$$

$$CH_6$$

$$C - CH_3$$

$$CH_6$$

$$C - CH_3$$

$$CH_7$$

$$C - CH_8$$

$$CH_8$$

$$C - CH_8$$

$$C -$$

$$\begin{array}{c} O \\ O \\ C \\ O \\ O \\ O \end{array}$$
 (A)

(a) 
$$OH \longrightarrow C - O - CH_3$$
 (b)  $OH \longrightarrow C - O - CH_3$  (c)  $OH \longrightarrow OH$  (d)  $OH \longrightarrow OH$ 

5. Predict the product when given compound (A, in the above question 4) reacts with NaBH<sub>4</sub>.

(a) 
$$OH \longrightarrow C - O - CH_3$$

6. 
$$C - O - H + CH_3 - O^{18} - H$$

$$(d) \stackrel{\text{OH}}{\longrightarrow} OH$$

Methyl benzoate

The labelled  $-O^{18}$  will be in :

- (a) H<sub>2</sub>O
- (c) Both (a) and (b)

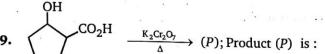
- (b) Methyl benzoate
- (d) Benzoic acid

7. 
$$CO_2H$$
  $CH_2 - OH$   
 $CO_2H$   $CH_2 - OH$   $CH_2 - OH$   $CH_2 - OH$   $CH_2 - OH$   $CH_2 - OH$ 

$$\begin{array}{c} O \\ \parallel & _{18} \\ C-O-CH_2 \\ (b) \mid & \mid \\ C-O-CH_2 \\ \parallel & _{18} \\ O \end{array}$$

- 8. Which is oxidized most easily?
  - (a)  $CH_3 CHOH CH_3$
  - (c) CH<sub>3</sub> CH<sub>2</sub> O CH<sub>2</sub> CH<sub>3</sub>

(d) 
$$CH_3$$
 OH



Which of the following react with HBr at faster rate?

$$CH_3 - CH \longrightarrow CH_2 - OH$$

Above conversion can be done by:

12. 
$$\underbrace{ \begin{array}{c} 2 \text{ CH}_3 \text{OH} \\ \text{H}_2 \text{SO}_4, \Delta \end{array}}_{\text{CO}_2 \text{H}} (A) \text{ ; Product } (A) \text{ is :}$$

ÒН

$$(d) \bigcirc C - CH_3$$

OH (*P*); Unknown (*P*) of the reaction is: 13.

(d) 
$$4$$
  $5$   $1$   $C$   $Ph$   $C$   $Ph$ 

**14.** Predict the major product of the given reaction.

(a) 
$$OMe$$

15. Identify the major product,

$$(a) \qquad (b) \qquad (c) \qquad (d) \qquad (d)$$

**16.**  $\stackrel{\text{H}^+}{\longrightarrow}$  (A); Product (A) is:

17.  $OCH_3$   $OCH_3$ LIAIH<sub>4</sub>  $\rightarrow$  (A) Major; product (A) is:

$$(a) \begin{picture}(60,0){\line(1,0){1300}} \put(0,0){\line(1,0){1300}} \put(0,0){\line(1,0){1300}$$

22. Consider the following alcohols,

(II) 
$$O_2N$$
 CH $_2OH$ 

(III) 
$$_{\mathrm{CH_3O}}$$
  $_{\mathrm{CH_2OH}}$ 

The order of decreasing reactivities of these alcohols towards nucleophilic substitution with HBr is:

(a) III > I > IV > II

VI < II < I < III (d)

(c) I > III > IV > II

(d) I > III > IV

23. 
$$0 \longrightarrow 0 \longrightarrow 0 \longrightarrow NaBH_4 \longrightarrow (P)$$

$$0 \longrightarrow 0 \longrightarrow 0 \longrightarrow 0 \longrightarrow (P)$$

Sum of number of 1° alcoholic groups in product (P) and (Q) is:

(a) 1

(b) 2

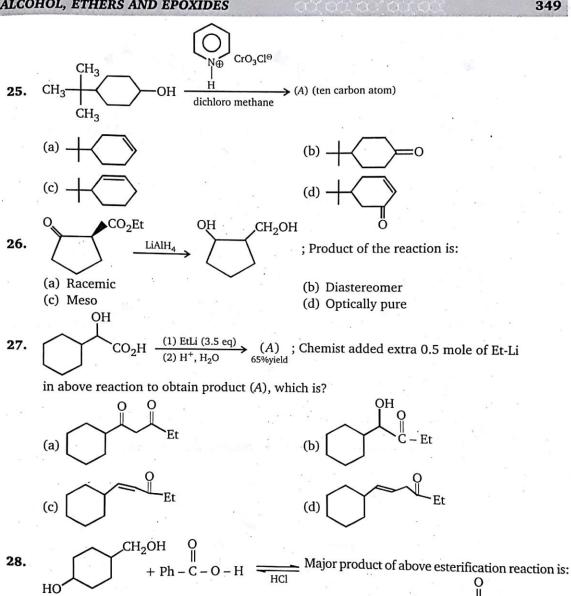
(c) 3

(d) 5

**24.** In presence of dil. HCl, compound *A* is converted to a constitutional isomer (*B*), compound *B* is:

(a) 
$$NH_2$$
 O - C  $NO_2$  (b)  $NH_2$  O - C  $NO_2$ 

(c) 
$$NH_2$$
 O - C  $NO_2$ 



(b)

(d)

HO

НО

HO

CH<sub>2</sub>-O-Ph

НО

- (a) S<sub>N1</sub>
- (b) S<sub>N<sup>2</sup></sub>
- (c) SN NGP
- (d) SN Ar

30. HO 
$$\xrightarrow{AC_2O}$$
  $\xrightarrow{AC_2O}$  (A); Product (A) of reaction is:

(b) NH<sub>2</sub>

(c) OH

31. 
$$CH_3 - C - OH$$

$$CH_3 - C - OH$$

$$CH_3$$

$$CH_3 - C - OH$$

$$CH_3$$

$$CH_3 - C - OH$$

$$CH_3$$

$$CH_3 - C - OH$$



(p) OF

(c) CO<sub>2</sub>H

(d) OH

**32.** Which is the best reagent to convert isopropyl alcohol to isopropyl bromide ?  $_{\text{CH}_3}^{\text{CH}_3}$   $_{\text{CH}_3}^{\text{CH}_3}$ 

$$\begin{array}{c|c}
CH_3 & CH_3 \\
 & | \\
CH_3 - CH - OH \xrightarrow{?} CH_3 - CH - Br
\end{array}$$

- (a) HBr
- (b) SOBr<sub>2</sub>
- (c) Br<sub>2</sub>
- (d) CH<sub>3</sub>MgBr

33. 
$$Ph \xrightarrow{\text{Ph}} OH \xrightarrow{\text{HNO}_2} A$$

Major product obtained in the above reaction is:

(a) 
$$Ph - C \xrightarrow{H} CH_3$$

(b) 
$$Ph - C - Y$$

(c) Racemic

(d) Diastereomers

34. 
$$OH \xrightarrow{HIO_4} (A) \xrightarrow{(1) \text{ LiAlH}_4 \text{ (excess)}} (B)$$

Total number of stereoisomers of product (B) will be:

(a) 2

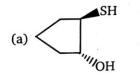
(b) 3

(c) 4

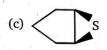
(d) 5

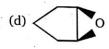
35. 
$$S - C - CH_3 \xrightarrow{1. HO^-} Major product of the reaction is :$$

$$O - C - CH_3$$



(b) OH





36. 
$$S - C - CH_3 \longrightarrow HO^{\Theta}$$

$$C - CH_3 \longrightarrow HO^{\Theta$$





CH<sub>3</sub>MgBr/H<sup>+</sup>

KMnO<sub>4</sub> (cold dil.) CrO<sub>3</sub>

 $H^+/\Delta$ 

(1)

(2)

(3)

(4)

For the above conversion the correct order of reagents used is:

(a) 
$$1 \rightarrow 2 \rightarrow 3 \rightarrow 4$$

(b) 
$$1 \rightarrow 4 \rightarrow 3 \rightarrow 2$$

(c) 
$$1 \rightarrow 4 \rightarrow 2 \rightarrow 3$$

(d) 
$$2 \rightarrow 3 \rightarrow 4 \rightarrow 1$$

38. 
$$CH_3$$
  $CH_2 - CH_3$   $CH_3$   $CH_$ 

Find missing reagents.

(a) 
$$x = \text{LiAlH}_4, y = \text{NaBH}_4$$

(b) 
$$x = \text{LiAlH}_4/\text{AlCl}_3$$
,  $y = \text{LiAlH}_4$ 

(c) 
$$x = \text{LiAlH}_4, y = \text{LiAlH}_4/\text{AlCl}_3$$

(d) 
$$x = H_2/Ni, y = H_2/Pt$$

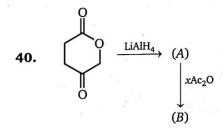
**39.** In solvolysis of 1, 2-dimethyl propyl p-toluene sulfonate in acetic acid at 75°C, (alkene + substitution products) will be formed by mechanism?

(a) 
$$S_{N^2}$$
,  $E_2$ 

(b) 
$$S_{N^2}$$
,  $E_1$ 

(c) 
$$S_{N^1}$$
,  $E_2$ 

(d) 
$$S_{N^1}$$
,  $E_1$ 



x = moles of anhydride consumed

- (a)
- (b) 2
- (c) 3
- (d) 4
- **41.** Identify product when (R) and (S) 2 butanol reacts with (R,R) tartaric acid in acidic medium.
  - (a) Racemic

(b) Diastereomer

(c) Meso

(d) Pure enantiomer

An alcohol of formula C<sub>9</sub>H<sub>12</sub>O reacts with Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form a compound having formula C<sub>9</sub>H<sub>10</sub>O. The original alcohol might be:

(a) 
$$\langle CH_2 - CH_2 - CH_2 - OH \rangle$$

(b) 
$$\sim$$
 CH - CH<sub>2</sub> - CH<sub>3</sub>

(c) 
$$CH_3$$

(d) 
$$CH_3$$
  $CH - CH_2OH$ 

43. An optically active alcohol of formula  $C_9H_{12}O_2$  produced the following compound when refluxed with KMnO4.

The original compound showed these properties also:

$$C_9H_{12}O_2 \xrightarrow{Na} H_2 \text{ liberated}$$

$$\xrightarrow{(A)} Br_2 \longrightarrow \text{ no rapid reaction}$$

$$\xrightarrow{CrO_3/H^+} C_9H_8O_3$$

What is structure of (A)?

- Which are not cleaved by HIO4?
  - I: glycerol
  - III: 1, 3-propenediol
  - (a) I, II, III, IV
  - (c) II, III

- II: glycol
- IV: methoxy-2-propanol
- (b) I, II
- (d) III, IV
- Which of the following reactions require an oxidising agent? 45.
  - (a)  $CH_3 CH = CH_2 \longrightarrow CH_3 CH_2 CH_3$
  - (b)  $CH_3 CH_2OH \longrightarrow CH_3CHO$
  - (c)  $CH_3 CH_2Cl \longrightarrow CH_3 CH_3$ (d)  $CH_3 CH_2OH \longrightarrow CH_3 CH_2Cl$
- What is the major product of the following reaction? 46.

$$\begin{array}{c}
\stackrel{\text{NaBH}_4}{\longrightarrow} \text{ product}
\end{array}$$

- **47.** Which of the esters shown, after reduction with LiAlH<sub>4</sub> and aqueous workup, will yield two molecules of only a single alcohol?
  - (a) CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- (b)  $C_6H_5CO_2CH_2C_6H_5$

(c)  $C_6H_5CO_2C_6H_5$ 

- (d) None of these
- **48.** For the following reaction, select the statement that best describes the change.

$$RCH_2OH + PCC [C_5H_5NH^+ClCrO_3^-] \longrightarrow$$

- (a) The alcohol is oxidized to an acid, and the Cr(VI) is reduced
- (b) The alcohol is oxidized to an aldehyde, and the Cr(VI) is reduced
- (c) The alcohol is reduced to an aldehyde, and the Cr(III) is oxidized
- (d) The alcohol is oxidized to a ketone, and the Cr(VI) is reduced
- 49. What is the product of the following reaction?

(a) Only 1

(b) 1:1 mixture of 2 and 3

(c) Only 2

- (d) 1:1:1 mixture of 1, 2, and 3
- **50.** An organic compound *B* is formed by the reaction of ethylmagnesium iodide (CH<sub>3</sub>CH<sub>2</sub>MgI) with a substance *A*, followed by treatment with dilute aqueous acid. Compound B does not react with PCC in dichloromethane. Identify *A*?

- (d) H<sub>2</sub>C CH<sub>2</sub>
- **51.** Which of the following reagents would carry out the following transformation? (D =  ${}^{2}$ H)

(a) NaBD<sub>4</sub> in CH<sub>3</sub>OH

(b) LiAlH<sub>4</sub>, then D<sub>2</sub>O

(c) NaBD<sub>4</sub> in CH<sub>3</sub>OD

- (d) LiAlD<sub>4</sub>, then D<sub>2</sub>O
- **52.** Which sequence of steps describes the best synthesis of 2-methyl-3-pentanone?

- (a) (1) 1-Propanol + (CH<sub>3</sub>)<sub>2</sub>CHMgBr, diethyl ether (2)  $H_3O^+$ (3) PCC, CH<sub>2</sub>Cl<sub>2</sub> (b) (1) 1-Propanol +  $Na_2Cr_2O_7$ ,  $H_2SO_4$ ,  $H_2O$ , heat (2) SOCl<sub>2</sub> (3) (CH<sub>3</sub>)<sub>2</sub>CHCl, AlCl<sub>3</sub>
- (c) (1) 1-Propanol + PCC, CH<sub>2</sub>Cl<sub>2</sub> (2) (CH<sub>3</sub>)<sub>2</sub>CHLi, diethyl ether (3)  $H_3O^+$ 
  - (4) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, heat
- (d) (1) 2-Propanol +  $Na_2Cr_2O_7$ ,  $H_2SO_4$ ,  $H_2O$ , heat
  - (2) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Li, diethyl ether
  - (3)  $H_3O^+$

(a) I and II

(a) 5, 6, 7

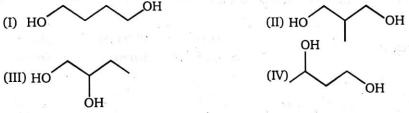
- (4) PCC, CH<sub>2</sub>Cl<sub>2</sub>
- Diols (I-IV) which react with CrO<sub>3</sub> in aqueous H<sub>2</sub>SO<sub>4</sub> and yield products that readily under 53. go dercarboxylation on heating, are:

(c) II and IV

(c) 6, 7

(d) I and IV

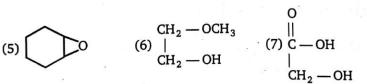
(d) 3, 4, 5, 6, 7



(b) II and III Which of following compounds are not oxidized by HIO4? 54.

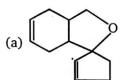
$$CH_3 - CH - OH$$
  $CH_3 - C = O$   
 $CH_2 - OH$   $CH_2 - C = O$   $CH_3 - C = O$ 

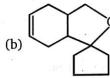
$$CH_3 - C = 0$$
  $CH_3 - C = 0$   $CH_3 - C = 0$   $CH_3 - C = 0$   $CH_3 - CH - NH_2$ 

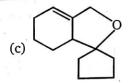


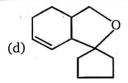
(b) 4, 5, 6, 7

55. 
$$CH_2OH \xrightarrow{TsCl} (A) \xrightarrow{B0^{\circ}C} (B) 84\%$$
; Final product (B) will be :

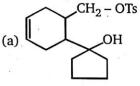


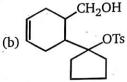


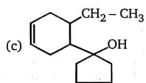


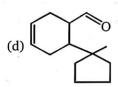


56. Unknown (A) in the reaction (given in Q. 55) is:









57. In the given table, identify the incorrect option. The digit in box indicate the moles of that substance.

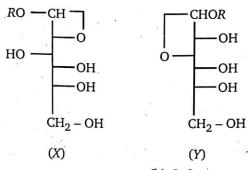
Reactant	HIO <sub>4</sub> consumed	HCO <sub>2</sub> H formed	HCHO formed
OH $\mid$ (a) HO – CH $_2$ – CH– CH $_2$ – OH	2	1	2
OH OH OH 	3	2	1
$\begin{array}{cc} & \text{OCH}_3\\ &  \\ \text{(c)} & \text{HO}-\text{CH}_2-\text{CH}-\text{CH}_2\text{OH} \end{array}$	0	0	0
OH OCH $_3$ (d) HO – CH $_2$ – CH– CH $_2$	1	1	1

Succinic acid  $\xrightarrow{\Delta}$  (A)  $\xrightarrow{NH_3}$  (B)  $\xrightarrow{Br_2}$  (C); Product (C) will be: 58.

(c) 
$$|$$
 CH<sub>2</sub> - NH<sub>2</sub>

$$CH_2 - CO_2H$$
  
(d) |  $CH_2 - CH_2 - Br$ 

**59A.** Given are the structures of cyclic D-glucoside. Moles of HIO<sub>4</sub> consumed with X and Y are ...... respectively:



- (a) 2, 2
- (c) 2, 3

- (b) 3, 3
- (d) 3, 2
- **B.** Moles of formic acid formed in *X* and *Y* respectively are:
  - (a) 1, 2

(b) 2, 1

(c) 2, 3

- (d) 3, 2
- C. Moles of HCHO formed are:
  - (a) 1, 1

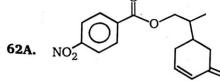
(b) 2, 2

(c) 1, 2

- (d) 2, 1
- 60. In which of the following group, each member gives positive iodoform test?
  - (a) methanol, ethanol, propanone
- (b) ethanol, isopropanal, methanal(d) propanal, propanol-2, propanone
- (c) ethanol, ethanal, isopropyl alcohol  $H_2O^{18} + Na \longrightarrow (A) + (B)$ 
  - $\begin{array}{c}
    O \\
    || \\
    CH_3 C O CH_2 CH_3 + (A) \longrightarrow (C) + (D) \text{ alcohol}
    \end{array}$

Product (C) of the reactions is:

(d) 
$$CH_3 - C - O^{\Theta}N_a^{\Theta}$$



 $\xrightarrow{\text{(Ph}_3\text{P)}_3 \text{ RhCl}} (A) \xrightarrow{\text{0.1 M NaOH}} (B) + (C)$   $\xrightarrow{\text{(Ph}_3\text{P)}_3 \text{ RhCl}} (A) \xrightarrow{\text{(Contains no nitrogen)}} (B)$ 

Product (B) of the reaction is:

$$(a) \bigcirc OH$$

$$(b) \bigcirc OH$$

$$NO_{2}$$

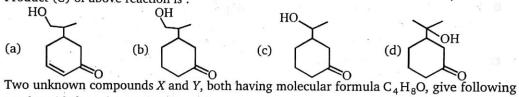
$$(c) \bigcirc OH$$

$$NO_{2}$$

$$(d) \bigcirc OH$$

$$NO_{2}$$

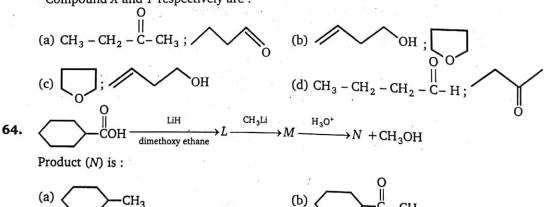
B. Product (C) of above reaction is:



63. results with four chemical tests.

Shide a Co	Bromine	Na metal	Chromic acid	Lucas reagent
Compound X	decolourises	bubbles	Orange to Green	No reaction
Compound Y	No reaction	No reaction	No reaction	No reaction

Compound X and Y respectively are:



**65.** Assign the structure of major product (*X*) of the reaction given below.

$$(a) \longrightarrow CH - COH \longrightarrow CH_3CH_2OH \longrightarrow SOCl_2 \longrightarrow (X)$$

$$(a) \longrightarrow CH - C - OH \longrightarrow (b) \longrightarrow CH - C - OEt$$

$$(c) \longrightarrow CH - C - CI \longrightarrow (d) \longrightarrow CH = CH - C - O - Et$$

$$(c) \longrightarrow CH - C - OCH_2 - CH_3 + CH_3 - COH \longrightarrow (A) + (B)$$

$$(d) \longrightarrow CH - C - OCH_2 - CH_3 + CH_3 - COH \longrightarrow (A) + (B)$$

$$(d) \longrightarrow CH - C - OCH_2 - CH_3 + CH_3 - COH \longrightarrow (A) + (B)$$

$$(d) \longrightarrow CH - C - OH, CH_3 - C - OCH_2CH_3$$

$$(e) \longrightarrow CH - C - OH, CH_3 - C - OCH_3$$

$$(f) \longrightarrow CH - G - OEt, CH_3 - C - OH$$

$$(g) \longrightarrow CH - G - OEt, CH_3 - C - OH$$

$$(g) \longrightarrow CH - G - OEt, CH_3 - C - OH$$

$$(g) \longrightarrow CH - C - OCH_3 + CH_3CH_2OH \longrightarrow (A) + CH_3OH \longrightarrow (A) +$$

In above reaction molecular formula of glycerol increases by :

- (a)  $C_4H_4O_2$
- (b)  $C_6H_6O_6$
- (c)  $C_6H_6O_2$
- (d)  $C_6H_6O_3$

**69.** Give the best conditions for this transformation:

$$H_3C$$
  $OCH_3$   $OCH_3$ 

- (a) CH<sub>3</sub>OH, H<sup>+</sup>(cat.), heat
- (b) H<sub>2</sub>O, H<sup>+</sup> (cat.), heat

(c) Mg, ether, CH<sub>3</sub>OH

- (d) SOCl<sub>2</sub>, CH<sub>3</sub>OH
- **70.** Give the major organic product of the following reaction.

(a) 
$$(2) \text{ H}_2\text{O}, \text{H}^+ \text{ to neutralize}$$

$$(b) \qquad \qquad (d)$$

$$(c) \qquad \qquad (d)$$

Product (D) in above reaction is:

72. Select the best method for the preparation of the following compounds:

(MCPBA = Metachloro per benzoic acid )

- (a) reaction of cyclohexanone with CH3Li
- (b) reaction of 1-methylcyclohexene with Hg(OAc)2 followed by NaBH4
- (c) reaction of cyclohexene with BH<sub>3</sub>; NaOH/H<sub>2</sub>O<sub>2</sub>, following by CH<sub>3</sub>Br
- (d) reaction of cyclohexene with MCPBA, followed by CH<sub>3</sub>MgBr
- **73.** Identify the reagents (1-4), required for the transformations shown and arrange them in correct order.

- (1) LAH (LiAlH<sub>4</sub>)
- (3) NaIO<sub>4</sub>
- (a)  $1 \rightarrow 3 \rightarrow 4 \rightarrow 2$
- (c)  $2 \rightarrow 1 \rightarrow 3 \rightarrow 4$

- (2) OsO<sub>4</sub>
- (4) NaBH<sub>4</sub>
- (b)  $2 \rightarrow 3 \rightarrow 1 \rightarrow 4$
- (d)  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$
- 74. Which describes the best stereochemical aspects of the following reaction?

$$Ph \xrightarrow{CD_3} \xrightarrow{H-Br} Produc$$

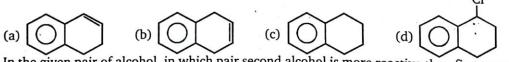
- (a) Inversion of configuration occurs at the carbon undergoing substitution.
- (b) Retention of configuration occurs at the carbon undergoing substitution.
- (c) Racemization (loss of configuration) occurs at the carbon undergoing substitution.
- (d) The carbon undergoing substitution is not stereogenic
- 75. Which of following is an example of Pinacol-Diazotization?

(a) 
$$Me_2C - CMe_2 \xrightarrow{Ag^+} Me - C - CMe_3$$
 (b)  $Me_2C - CMe_2 \xrightarrow{NaNO_2} Me - C - CMe_3$ 
OH Br
OH NH<sub>2</sub>

(c) 
$$Me_2C - CMe_2 \xrightarrow{H^{\oplus}} Me - C - CMe_3$$
 (d)  $R$   $R$   $R$   $R$   $R$ 

- **76.**  $(A) \xrightarrow{H_3O^9} B + C$ ; (B) and (C) both give +ve iodoform test. Compound (A) is:
  - (a)  $CH_3 CH = CH O CH_2 CH_3$  (b)  $CH_3 C O CH_2 CH_3$   $CH_3$
  - (c)  $CH_3 C O CH_2 CH_3$  (d) both (b) and (c)  $CH_2$
- 77. A solution of  $Ph_3CCO_2H$  in conc.  $H_2SO_4$  gives (X) when poured into methanol X is :
  - O O || (a)  $Ph_3C C O CH_3$  (b)  $Ph_2CH C O CH_3$  (c)  $Ph_3C OCH_3$  (d)  $Ph_3C CH_3$

Product (B) of the above reaction is:



- 79. In the given pair of alcohol, in which pair second alcohol is more reactive than first towards hydrogen bromide?
  - (a)  $\stackrel{\text{CH}_3}{\longrightarrow}$  OH and  $\stackrel{\text{CH}_3}{\longrightarrow}$  (b)  $\stackrel{\text{OH}}{\longrightarrow}$  and  $\stackrel{\text{CH}_4}{\longrightarrow}$  CH CH<sub>3</sub>
    (c) CH<sub>3</sub> CH CH<sub>2</sub> CH<sub>3</sub> and CH<sub>3</sub> CH<sub>2</sub> CH CH<sub>2</sub> OH  $\stackrel{\text{CH}_3}{\longrightarrow}$  CH<sub>3</sub>

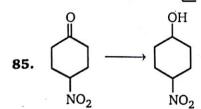
(d) 
$${\rm CH_3-CH-CH_2-CH_3}$$
 and  ${\rm (CH_3)_2C-CH_2-CH_3}$  OH

- 80. Rank the transition states that occur during the following reaction steps in order of increasing stability (least → most stable)
  - 1.  $H_3C \longrightarrow \dot{O}H_2 \longrightarrow CH_3^+ + H_2O$
  - 2.  $(CH_3)_3C \dot{O}H_2 \longrightarrow (CH_3)_3C^+ + H_2O$
  - 3.  $(CH_3)_2CH \longrightarrow (CH_3)_2CH^+ + H_2O$
  - (a) 1 < 2 < 3
- (b) 2 < 3 < 1 (c) 1 < 3 < 2
- (d) 2 < 1 < 3
- $\xrightarrow{MnO_2}$  (A), Product (A) is: 81.
- (b) HO'

- In which of the following reactions hydrogen gas will not be evolved? 82.
  - (a)  $CH_3 CH_2 OH \xrightarrow{Na}$
- (b)  $CH_3 CH_2 OH$
- (c)  $CH_3 CH OH \xrightarrow{Al}$
- (d) CH<sub>3</sub> CH OH | CH<sub>3</sub>
- $\xrightarrow{\text{PBr}_3}$  (C)  $\xrightarrow{\text{Mg, ether}}$  Grignard reagent 83.

When Grignard reagent reacts with (B) product  $(\tilde{D})$  will obtained. Reactant (A) of the above reaction is:

- ; structure of (A) is : 2(B)(Chiral alcohol only)
  - Et
- Et



Above conversion can be acheived by:

(a) LiAlH<sub>4</sub>

(Mandelic acid)

(b) NaBH<sub>4</sub>

(c) H<sub>2</sub>/Ni

(d) CrO<sub>3</sub>

86.

$$\begin{array}{c|c}
OH & O \\
\parallel & \parallel \\
CH - COH
\end{array}$$
+ EtOH  $\xrightarrow{HCl}$  (86%)

Identify product of above Fischer esterification reaction:

O - Et  

$$\mid$$
  
(a) Ph - CH - CO<sub>2</sub>H

87.

$$CH_3 \xrightarrow{CH_2CH_2COH} \xrightarrow{CH_3Li} (A) \xrightarrow{CH_3Li} (B) \xrightarrow{H_3O^{\oplus}} (C)$$

Product (C) of the above reaction is:

O OH OH OH OH (a) 
$$CH_3 - C - CH_2 - CH_2 - C - CH_3$$
 (b)  $CH_3 - C - CH_2 - CH_2 - C - CH_3$   $CH_3$   $CH_3$ 

(b) 
$$CH_3 - C - CH_2 - CH_2 - C - CH_3$$
  
 $CH_3 - CH_3 - CH_3$ 

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

88. What is the major product of the following reaction?

$$\begin{array}{c} \text{OH} \\ \mid \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{OH} \xrightarrow{\text{CrO}_3} \text{Product} \end{array}$$

OH O 
$$\parallel$$
 (a)  $CH_3$  - $CH$  - $CH_2$  - $C-H$ 

- 89. The major reason that phenol is a better Bronsted acid than cyclohexanol is that:
  - (a) it is a better proton donor.
  - (b) the cyclohexyl group is an electron donating group by induction, which destabilizes the anion formed in the reaction by resonance.
  - (c) phenol is able to stabilize the anion formed in the reaction.
  - (d) the phenyl group is an electron withdrawing group by induction, which stabilizes the anion formed in the reaction.
- 90. Which of these reagents would accomplish the following reduction?

$$N \equiv C - CH_2 - C - CH_2 - CH = CH_2 \longrightarrow N \equiv C - CH_2 - CH_2 - CH = CH_2$$

(a) NaBH<sub>4</sub>

- (b) LiAlH<sub>4</sub> (d) H<sub>2</sub>O<sup>+</sup>
- (c) 1 mole H<sub>2</sub>, poisoned catalyst, low pressure
- 91.

$$\xrightarrow{\text{MnO}_2}$$
 (B)

Identify A and B:

(a) 
$$A = \text{NaBH}_4$$
,  $B = \bigcirc$ 

(b) 
$$A = \text{NaBH}_4$$
,  $B = \bigcirc$ 

(c) 
$$A = \text{LiAlH}_4, B = \bigcirc$$

(d) 
$$A = \text{LiAlH}_4, B =$$

92. Ph 
$$-CH_2 - CH - CH_3 \xrightarrow{K} \xrightarrow{C_2H_5Br} (A)$$
  
OH

Product (A) in above reaction is:

- (a) Ph CH<sub>2</sub> –CH –CH<sub>3</sub>, (inversion) OEt
- (b) Ph -CH<sub>2</sub> -CH -CH<sub>3</sub>, (retention)
  OEt
- (c) Ph CH<sub>2</sub> -CH -CH<sub>3</sub>, (racemic)
  OEt
- (d)  $Ph CH = CH CH_3$

93. Ph 
$$-C-O-H+CH_3-O^{18}-H \xrightarrow{H^+} (X)+H_2O$$
; Identify X:

(a) 
$$X = Ph - C - O^{18} - CH_3$$
 (Trans esterification)

(b) 
$$X = Ph - C - O^{18} - CH_3$$
 (Esterification reaction)

(c) 
$$X = Ph - C - O^{18} - CH_3$$
 (Saponification)

(d) 
$$X = Ph - C - O - CH_3$$
 (Hydrolysis)

**94.** 
$$R - OH + H - O - C$$
  $\longrightarrow$   $NO_2 \xrightarrow{H^*} R - O - C$   $\longrightarrow$   $NO_2$ 

Fastest rate of reaction will be when R is:

- 95. Select the correct statement.
  - (a) Solvolysis of (CH<sub>3</sub>)<sub>2</sub>C = CH CH<sub>2</sub> Cl in ethanol is over 6000 times greater than alkyl chloride (25°C)
  - (b)  $CH_3 CH = CH CH_2 OH$  when reacts with HBr give a mixture of 1-bromo-2-butene and 3-bromo 1-butene
  - (c) When solution of 3-buten-2-ol in aqueous sulphuric acid is allowed to stand for one week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol
  - (d) All of these

96. 
$$OH \longrightarrow CH_2 - OH \longrightarrow OH$$

Above transformation can be carried out by:

(a)  $H^+/\Delta$ , Zn(Hg), HCl

(b) HIO<sub>4</sub>, LiAlH<sub>4</sub>

(c)  $\text{HIO}_4, \text{H}^+/\Delta$ 

(d)  $H^+/\Lambda$  HIO

97. 
$$H_2C = CH - CH_2 - CH_2 - CH_3 \xrightarrow{SOCl_2} (A) \xrightarrow{O_3/Zn} (B) \xrightarrow{NaBH_4} (C)$$

Compound (C) is:

OH (a) 
$$CH_3$$
 - $CH$  - $CH_2$  - $CH$  - $CH_3$  Cl

(b) 
$$HOCH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2$$

(d) 
$$HO - CH_2 - CH_2 - CH_2 - CH_3 - CH_3$$

98. Iodoform can be obtained on warming NaOH and iodine with:

(a) CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub>

(b) (CH<sub>3</sub>)<sub>2</sub>CHCC<sub>2</sub>H<sub>5</sub>

(c) CH<sub>3</sub> — C — OCH<sub>3</sub>

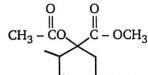
- (d) (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH
- 99. Which of these is a reducing agent?
  - (a)  $CrO_3/H^+$

(b) KMnO<sub>4</sub>

(c) LiAlH<sub>4</sub>

- (d)  $O_3$
- 100.  $(i). (BH_3)_2 \longrightarrow (P)$ ; Product (P) in the reaction is:
  - (a) СН<sub>2</sub>ОН (b) СН<sub>3</sub>ОН
- (c)  $\bigcirc$   $\bigcirc$   $\bigcirc$   $\bigcirc$   $\bigcirc$   $\bigcirc$
- (d) OH
- 101.  $CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{Na_2Cr_2O_7 \atop COOl} (P)$ ; Product (P) in the reaction is:
  - $CH_3$  |(a)  $CH_3 - C = CH_2$

- (b) CH<sub>3</sub> —CH —CH<sub>3</sub>
- (c)  $CH_3 CH_3 CH_3$  $CH_3 - CH_3 - CH_3$
- (d) No reaction
- 102. 1, 2, 3 butanetriol undergoes oxidative cleavage of HIO<sub>4</sub>. During this process
  - (a) 1 equivalent of HIO<sub>4</sub> consumed & HCO<sub>2</sub>H & H<sub>3</sub>C C-CO<sub>2</sub>H are formed
  - (b) 2 equivalents of HIO<sub>4</sub> consumed & HCO<sub>2</sub>H, HCH = O & CH<sub>3</sub> CH = O are formed
  - (c) 3 equivalents of HIO<sub>4</sub> consumed & HCO<sub>2</sub>H (2 eq.) & 1 eq. of CH<sub>3</sub>CO<sub>2</sub>H are formed
  - (d) 2 equivalents of HIO<sub>4</sub> consumed & 2 eq. of HCO<sub>2</sub>H & 1 eq. of CH<sub>3</sub>CH = O is formed



103.

 $(i) \stackrel{\text{LiAlH}_4}{\text{(ii) H}_2\text{O}} \rightarrow (A)$ ; Product (A) of the reaction is:



- (b) CH<sub>2</sub> OH
- (c) OH CH<sub>2</sub>OH

104. 
$$R - C - O - R' + R''OH \xrightarrow{H^{\oplus}} R - C - O - R'' + R'OH$$

Above reaction is/an example of:

(a) esterification

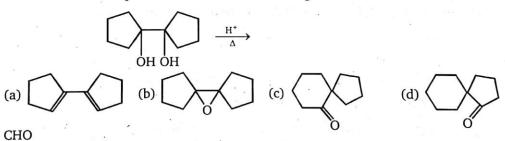
(b) saponification

(c) trans-esterification

- (d) hydrolysis
- 105. What is the major organic product of the following sequence of reactions?

$$(CH_3)_2CHCH_2OH \xrightarrow{PBr_3} \xrightarrow{Mg} \xrightarrow{H_2C - CH_2} \xrightarrow{H_3O^+} ?$$

- (a) (CH<sub>3</sub>)<sub>2</sub> CHCHCH<sub>2</sub>CH<sub>3</sub>
- (b) (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OH
- (c) (CH<sub>3</sub>)<sub>2</sub> CHCH<sub>2</sub>CHCH<sub>3</sub>
- (d) (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
- **106.** The structure of the product formed in the reaction given below is:



Products obtained in the above reaction are:

- CH<sub>2</sub> -OH
- (a) HCHO, HCO<sub>2</sub>H

(b) HCHO, 2HCO<sub>2</sub>H

(c)  $CO_2$ ,  $2HCO_2H$ 

(d) CO2, HCHO, HCO2H

ÇНО

**108.**  $(CH - OH)_3 + 4HIO_4 \longrightarrow Products obtained are :$ 

CH<sub>2</sub> -OH

Aldo pentose

(a) 4HCO<sub>2</sub>H, HCHO

(b) 4CH<sub>2</sub>O, HCO<sub>2</sub>H

(c) CO<sub>2</sub>, 4HCHO

(d) CO<sub>2</sub>, 3HCO<sub>2</sub>H, HCHO

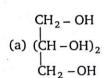
CH<sub>2</sub>OH

109. (i) 
$$(CH - OH)_3 \xrightarrow{4HIO_4} Product$$
 $CH_2 - OH$ 

(ii) 
$$(CH - OH)_4 \xrightarrow{5HIO_4} Product$$
  
 $CH_2 - OH$ 

Ratio of moles of formic acid obtained in reaction (i) and reaction (ii) is:

- (a) 3/4
- (b) 4/5
- (c) 1
- (d) 5/4
- 110. Which of the following compound gives 2HCHO, CO<sub>2</sub>, HCO<sub>2</sub>H when oxidised by periodic acid?



- CHO | (b) (CH – OH)<sub>2</sub> | | | CH<sub>2</sub> – OH
- $CH_2 OH$  C = O  $(c) \mid CH OH)_2$   $CH_2 OH$
- CHO | C = 0 (d) | CH - OH | CH<sub>2</sub> - OH
- 111. Hydration of 3-phenylbut-1-ene in dil. H<sub>2</sub>SO<sub>4</sub> will give mainly:
  - (a) 3-Phenylbutan-1-ol

(b) 3-Phenylbutan-2-ol

(c) 2-Phenylbutan-2-ol

- (d) 2-Phenylbutan-1-ol
- 112. Decarboxylation of sodium salicylate with soda lime forms:
  - (a) Salicylic acid
- (b) Phenol
- (c) Benzene

 $\rightarrow$  What is the maximum value of (x)?

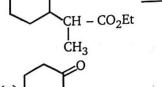
(d) None of these

(a) 1

(b) 2

CH2-OH

- (c) 3
- (d) 4



СН<sub>2</sub> – СН – ОН

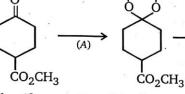
(b) 
$$CH - CH_2 - OH$$
 $CH_3$ 

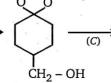
115. (A) + 
$$CH_2$$
 -  $OH$   $\xrightarrow{Pyridine}$   $CH_2$  -  $O$   $C = O$ ;  $CH_2$  -  $OH$ 

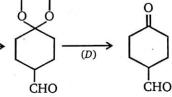
Reactant A of the above reaction is :

(b) COCl<sub>2</sub>









Identify correct combination:

$$(a) (A) = \begin{vmatrix} CH_2 - OH \\ CH_2 - SH \end{vmatrix}$$

(c) 
$$(C) = \text{KMnO}_2$$

(b) 
$$(B) = \text{NaBH}_4$$
 (c)  $(C) = \text{KMnO}_4$  (d)  $(D) = \text{H}_3\text{O}^{\oplus}$ 

- In the Libermann's nitroso reaction, sequential changes in the colour of phenol occurs as: 117.
  - (a) Brown or red  $\longrightarrow$  green  $\longrightarrow$  deep blue (b) Red  $\longrightarrow$  deep blue  $\longrightarrow$  green
  - (c) Red  $\longrightarrow$  green  $\longrightarrow$  white
- (d) White  $\longrightarrow$  red  $\longrightarrow$  green
- Ethanol when reacts with PCl<sub>5</sub> gives A, POCl<sub>3</sub> and HCl. A reacts with dry Ag<sub>2</sub>O to form 118. B(major product) and AgCl. A and B respectively are:
  - (a)  $C_2H_5Cl$  and  $C_2H_5OC_2H_5$
- (b)  $C_2H_4$  and  $C_2H_5OC_2H_5$ (d)  $C_2H_6$  and  $C_2H_5NO_2$
- (c) C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>

119. 
$$CH_3 - (CH_2)_3 - OH \xrightarrow{CH_3 - \stackrel{!}{|}-Cl} (A) \xrightarrow{KCN} (B) \xrightarrow{H_3O^{\oplus}} (C)$$

Product (C) is:

(a) 
$$CH_3 - (CH_2)_3 - CO_2H$$

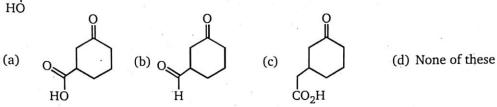
(b) 
$$CH_3 - (CH_2)_3 - ^{14}CO_2H$$

Choose the best synthesis of phenyl *n*-propyl ether. 120.

## ALCOHOL, ETHERS AND EPOXIDES

371

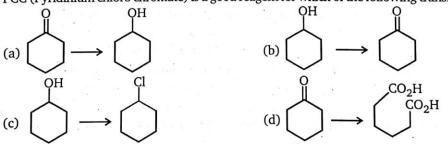
121.  $\xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4}$  The product obtained is:



**122.** What is true for the equilibrium reaction?

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OH + CH_3 - OH \end{array} \xrightarrow{\operatorname{cat.}} \begin{array}{c} O \\ \parallel \\ CH_3 - C - O - CH_3 + H_2OH \end{array}$$

- (a) The use of equimolar quantities of CH<sub>3</sub>OH and CH<sub>3</sub>COOH will give the greatest yield of the ester at equilibrium
- (b) Removal of water will increase the amount of ester at equilibrium
- (c) Addition of CH<sub>3</sub>COOCH<sub>3</sub> will cause the formation of equal an equal number of moles of water
- (d) Application of pressure increases the amount of ester at equilibrium
- 123. PCC (Pyridinium chloro chromate) is a good reagent for which of the following transformations?



- 124. How many primary alcohols (including stereoisomers) are possible with formula C<sub>5</sub>H<sub>12</sub>O?
  - (a) Two

(b) Three

(c) Four

- (d) Five
- 125. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with the product obtained in the reaction between:
  - (a) CH<sub>3</sub>I and Mg

(b) C<sub>2</sub>H<sub>5</sub>I and Mg

(c) CH3Br and AlCl3

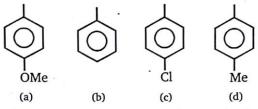
(d) CH<sub>3</sub>OH and ZnCl<sub>2</sub>

- **126.** 0.092 g of a compound with the molecular formula C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>on reaction with an excess of CH<sub>3</sub>MgI gives 67.00 mL of methane at STP. The number of active hydrogen atoms present in a molecule of the compound is :
  - (a) one

(b) two

(c) three

- (d) four
- **127.** Migratory aptitude of the following in decreasing order is:



(a) a > c > b > d

(b) a > d > b > c

(c) a > d > c > b

- (d) b > c > a > b
- 128. The major product formed in the reaction is:

(a) 
$$CH_2R \xrightarrow{H_3O^+}$$
?

(b)  $CH_2R$ 

(c)  $CH_2R \xrightarrow{H_3O^+}$ ?

(d)  $CH_2R$ 

(e)  $CH_2R \xrightarrow{H_3O^+}$  (d)  $CH_2R$ 

- **129.** Reaction of *R*-2-butanol with *p*-toluenesulphonyl chloride in pyridine then LiBr gives :
  - (a) R-2-butyl bromide

(b) S-2-butyl tosylate

(c) R-2-butyl tosylate

- (d) S-2-butyl bromide
- 130. Optically active 2-octanol rapidly loses its optical activity when exposed to:
  - (a) dilute acid
- (b) dilute base
- (c) light
- (d) humidity
- **131.** If (±) 2-methyl butanoic acid were esterified by reaction with (±) 2-butanol, how many optically active compounds would be present in the final equilibrium reaction mixture?
  - (a) 2
- (b) :
- (c) 4
- (d) e

Product Z of above reaction is:

 $\xrightarrow{\text{LIAIH}_4}$  (A); Identify the product:

(a) No reaction

134. 
$$(EtO)_2$$
CHCHO + CH<sub>3</sub>MgI  $\xrightarrow{H_3O^{\oplus}}$  (A)

Product obtained in the above reaction is:

(a) 
$$CH_3 - C - C - H$$

(c) 
$$CH_3 - C - CH_2 - OH$$

(d) 
$$CH_3 - CH - CH_2 - OH$$

135. Reaction - (1): 
$$CH_3 - CH = CH - CH_3 \xrightarrow{KMnO_4} (A) \xrightarrow{NalO_4} (B)$$
 2 mole

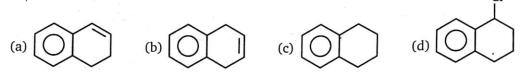
**Reaction - (2):**  $CH_3 - CH = CH - CH_3 \xrightarrow{KMnO_4/NalO_4} (C)$  2 mole

Product (B) and (C) respectively are:

(a) CH<sub>3</sub>CHO, CH<sub>3</sub>CO<sub>2</sub>H

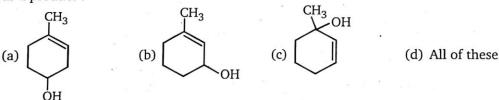
- (b) CH<sub>3</sub>CO<sub>2</sub>H, CH<sub>3</sub>CHO
- (c) CH3CHO in both reaction
- (d) CH<sub>3</sub>CO<sub>2</sub>H in both reaction

136. 
$$\xrightarrow{\text{TsCl}} A \xrightarrow{\text{LiAlH}_4} B ; \text{ Product } (B) \text{ is :}$$

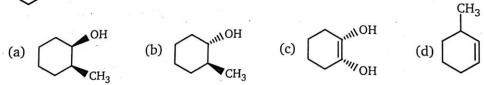


- **137.**  $\longrightarrow$  HO (CH<sub>2</sub>)<sub>6</sub> OH, this conversion can be achieved by
  - (a) O<sub>3</sub>, Zn, then LiAlH<sub>4</sub>

- (b) O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, then LiAlH<sub>4</sub>
- (c) cold dil. KMnO<sub>4</sub>, HIO<sub>4</sub>, then LiAlH<sub>4</sub>
- (d) All of these
- **138.** Which of the following alcohol on treatment with HCl give 3-chloro-3-methyl cyclohexene as a product?



139.  $(a) RCO_3 H \longrightarrow (A); Product of the reaction is:$ 

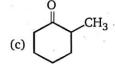


**140.** Esterification (shown below) is a reaction converting a carboxylic acid to its ester. It involves only the carbonyl carbon. Esterification of (–) -lactic acid with methanol yields (+)-methyl lactate. Assuming that there are no side reactions, what is true about this reaction?

- (a) An S<sub>N2</sub> process has occurred, inverting the absolute configuration of the chiral center
- (b) An  $S_{N^1}$  reaction at the chiral center has inverted the optical rotation
- (c) A diastereomer has been produced; diastereomers have different physical properties including optical rotation
- (d) Optical rotation is not directly related to absolute configuration, so the change in sign of rotation is merely a coincidence

**141.** Which of the following sets of reagents, used in the order shown, would successfully accomplish the conversion shown?

- (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>MgBr; H<sub>3</sub>O<sup>+</sup>; PCC, CH<sub>2</sub>Cl<sub>2</sub>
- (b) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>MgBr; H<sub>3</sub>O<sup>+</sup>; H<sub>2</sub>SO<sub>4</sub>, heat PCC, CH<sub>2</sub>Cl<sub>2</sub>
- (c)  $(C_6H_5)_3 \stackrel{+}{P} \stackrel{-}{C} HCH_2CH_3, B_2H_6$ ;  $CH_3CO_2H$
- (d)  $(C_6H_5)_3 \stackrel{+}{P} \stackrel{-}{C} HCH_2CH_3$ ;  $H_2O$
- 142.  $CO_2Et \xrightarrow{(1) H_3O^+ \atop (2)\Delta}$  Product; Product of the reaction is:

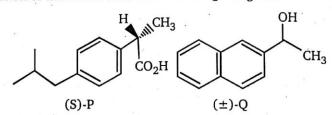


- **143.** Which of the following compound on hydrolysis followed by heating gives a product, which gives positive iodoform test?

O 
$$\parallel$$
(a)  $CH_3$  –  $CH$  –  $CH_2$  –  $CH_3$ 
 $CO_2$ Et

(b) 
$$\begin{array}{c|c} & CO_2Et \\ \hline & C-CH_3 \\ \hline & O \end{array}$$

- $(d) \xrightarrow{O} C O Et$
- 144. Treatment of a 2° OH with CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> yields an/a:
  - (a) aldehyde
- (b) carboxylic acid
- (c) ester
- (d) ketone
- 145. Esterification of the acid P with the alcohols Q will give :



- (a) only one enantiomer
- (b) a mixture of diastereomers
- (c) a mixture of enantiomers
- (d) only one diastereomer

146.  $EtO_2C$  O  $CO_2Et$  O Product

Identify major product of the reaction, when the given compound is hydrolysed and heated strongly:

147. RO—C find out the reactivity order with LiAlH<sub>4</sub>:

BCOCl

(a) A > B > C > D

(b) B > C > D > A

(c) D > C > B > A

(d) B > D > C > A

148. Find out the reaction in which obtained product give positive isocyanide test:

a) 
$$NH_2$$
 LiAlH<sub>4</sub> (b)  $NH_2$  NaBH<sub>4</sub>

(c) 
$$NH$$

$$O$$

$$NABH$$

$$O$$

$$NABH$$

In the above given compound how many functional group reduced by LAH (Lithium aluminium hydride ) and SBH (sodium borohydride) respectively ?

- (a) 4, 4
- (b) 4, 3
- (c) 3, 4
- (d) 4, 2

## ALCOHOL, ETHERS AND EPOXIDES

**150.** An unknown compound (A) (molarmass = 180) on acylation gives a product (molar mass = 390) than find the number of hydroxyl group present in compound (A).

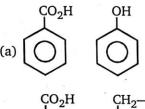
(a) 5

(b) 6

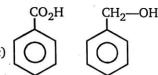
(c) 10

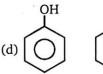
(d) 1

**151.** Which of the following compound is differentiated by NaHCO<sub>3</sub> as well as by NaOH?



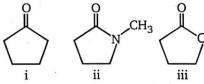
(b) OH CH<sub>2</sub>—OH







**152.** Arrange the following compounds in order of their reactivity toward LiAlH<sub>4</sub>.



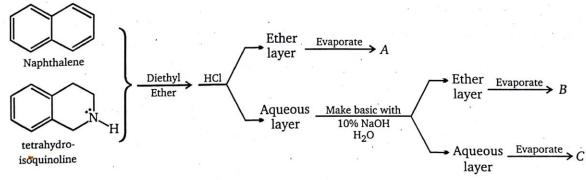
(a) i < ii < iii

(b) i < iii < ii

(c) ii < i < iii

(d) ii < iii < i

**153.** Choose the statement that is true about *A*, *B* and *C* in the following separation scheme.



- (a) A = tetrahydroisoquinoline, B = naphthalene and  $C = \text{inorganic ions such as Na}^+$  and  $Cl^-$
- (b) A = naphthalene, B = tetrahydroisoquinoline and  $C = \text{inorganic ions such as Na}^+$  and  $Cl^-$
- (c)  $A = \text{inorganic ions such as Na}^+$  and  $Cl^-$ , B = naphthalene and C = tetrahydroisoquinoline
- (d)  $A = \text{inorganic ions such as Na}^+$  and  $Cl^-$ , B = naphthalene and C = tetrahydroisoquinoline

154. 
$$CH_2$$
—OH  $\xrightarrow{xHI}$  value of  $x$  is :

- (a) 2
- (b) 3
- (c) 4
- (d) 5

OH

155. 
$$CO_2H$$
 $CH_2$ —CHO
 $(A) \xrightarrow{\text{NaBH}_4} (A) \xrightarrow{\text{H}^{\oplus}} (B)$ 
Cyclic

Compound (B) is:

- 1-Phenoxypropane is treated with excess of conc. HI at 0°C and the mixture of products is treated with thionyl chloride. The products formed are
  - (a) n-propanol + Chlorobenzene
- (b) Phenol + n-propyl iodide
- (c) n-propyl chloride + Chlorobenzene
- (d) n-propyl chloride + Phenol
- 157. Amongst the following compounds, the compound having the lowest boiling point is

						ANSV	WERS	— LE	VEL :	1					
1.	(c)	2.	(a)	3.	(b)	4.	(c)	5.	(b)	6.	(b)	7.	(b)	8.	(a)
9.	(b)	10.	(b)	11.	(b)	12.	(b)	13.	(a)	14.	(a)	15.	(a)	16.	(a)
17.	(d)	18.	(a)	19.	(b)	20.	(a)	21.	(a)	22.	(a)	23.	(d)	<b>24.</b>	(a)
25.	(b)	26.	(b)	27.	(b)	28.	(b)	29.	(c)	30.	(c)	31.	(b)	32.	(b)
33.	(a)	34.	(b)	35.	(b)	36.	(c)	37.	(c)	38.	(c)	39.	(d)	40.	(c)
41.	(b)	42.	(b)	43.	(d)	44.	(d)	45.	(b)	46.	(a)	47.	(b)	48.	(b)
49.	(a)	50.	(b)	51.	(a)	52.	(c)	53.	(c)	54.	(c)	55.	(b)	56.	(a)
57.	(d)	58.	(c)	59.	A-d	59.	B-b	59.	C-a	60.	(c)	61.	(c)	62.	A-b
62.	B-b	63.	(b)	64.	(c)	65.	(b)	66.	(a)	67.	(a)	68.	(d)	69.	(a)
70.	(c)	71.	(b)	72.	(d)	73.	(d)	74.	(c)	75.	(b)	76.	(d)	77.	(c)
78.	(c)	79.	(d)	80.	(c) ·	81.	(c)	82.	(d)	83.	(a)	84.	(b)	85.	(b)
86.	(c)	87.	(c)	88.	(b)	89.	(d)	90.	(a)	91.	(c)	92.	(b)	93.	(b)
94.	(a)	95.	(d)	96.	(b)	97.	(c)	98.	(a)	99.	(c)	100.	(a)	101.	(d)
102.	(b)	103.	(c)	104.	(c)	105.	(d)	106.	(c)	107.	(b)	108.	(a)	109.	(c)
110.	(d)	111.	(c)	112.	(b)	113.	(b)	114.	(b)	115.	(b)	116.	(d)	117.	(b)
118.	(a)	119.	(b)	120.	(a)	121.	(a)	122.	(b)	123.	(b)	124.	(d)	125.	(a)
126.	(c)	127.	(b)	128.	(c)	129.	(d)	130.	(a)	131.	(c)	132.	(b)	133.	(c)
134.	(b)	135.	(a)	136.	(c)	137.	(d)	138.	(d)	139.	(b)	140.	(d)	141.	(c)
142.	(b)	143.	(b)	144.	(d)	145.	(b)	146.	(c)	147.	(b)	148.	(a)	149.	(d)
150.	(a)	151.	(c)	152.	(d)	153.	(b)	154.	(b)	155.	(a)	156.	(b)	157.	(c)

anacarara



1. Consider the pairs of ethers, numbered I through V, shown below. To the right of each pair is a description of reaction conditions to be applied to each. One compound of the pair will react more rapidly than the other.

Which ether of the two will be more rapidly cleaved?

Write your answer in box.

	(A) Ether Pairs (B)	Cleavage Conditions
ı.	O—CH(CH <sub>3</sub> ) <sub>2</sub> & H <sub>3</sub> C H <sub>3</sub> C	Treated with HBr in CH <sub>3</sub> CN, 40°C
п.	$H_3C$ $O-C(CH_3)_3 & C_2H_5$ $O-CH_3$	Treated with H <sub>2</sub> SO <sub>4</sub> in CH <sub>3</sub> CN, 40°C
ш.	<b>△</b> -○- <b>△</b> & <b>△</b> -○- <b>△</b>	Treated with H <sub>2</sub> SO <sub>4</sub> in CH <sub>3</sub> CN, 40°C
IV.	CH <sub>3</sub> O OH OCH <sub>3</sub>	Treated with 5% aqueous H <sub>2</sub> SO <sub>4</sub> , 25°C
v	O/CH(CH <sub>3</sub> ) <sub>2</sub> & O/CH(CH <sub>3</sub> ) <sub>2</sub>	Treated with 5% aqueous H <sub>2</sub> SO <sub>4</sub> , 25°C

### 2. Comprehension

(a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH_2$$

(a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$$
 (b)  $CH_3 - CH_2 - CH_2 - CH_3 - CH_3 - CH_2 - CH_3 - C$ 

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

$$\begin{array}{c} \operatorname{CH_3} \\ \mid \\ (\operatorname{d}) \operatorname{CH_3} - \operatorname{CH_2} - \operatorname{C} - \operatorname{OH} \\ \mid \\ \operatorname{CH_3} \end{array}$$

$$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{(e) CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{OH} \end{array}$$

$$\begin{array}{c} \operatorname{CH_3} \\ \mid \\ \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH} - \operatorname{CH}_3 \\ \mid \\ \operatorname{OH} \end{array}$$

$$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{(g) HO-CH}_2\text{-CH-CH}_2\text{-CH}_3 \end{array}$$

$$\begin{array}{c} \operatorname{CH_3} \\ \mid \\ \operatorname{Ch_3} - \operatorname{C} - \operatorname{CH_2} - \operatorname{OH} \\ \mid \\ \operatorname{CH_3} \end{array}$$

Above compounds (a) to (h) are isomers of  $C_5H_{12}O$ .

Based on the above isomer answer the following (A to F).

- Which isomer is most reactive towards dehydration by conc. H2SO4? A.
- Which isomer will undergo rearrangement when treated with conc. H2SO4? В.
- Which isomers on dehydration with conc. H2SO4 give alkene which is capable to show C. geometrical isomerism?
- Which isomer is least acidic? D.
- Which isomers on dehydration give most stable alkene? E.
- Which isomer on dehydration with conc. H<sub>3</sub>PO<sub>4</sub> undergo maximum rearrangement? F.

## 3. Comprehension

$$[O] = Oxidation$$

Consider the above sequence and answer A to F.

- **A.** Conversion  $(CH_3 CH_3 \longrightarrow CH_3 CH_2 OH)$  alkane  $\longrightarrow$  alcohol is achieved by:
  - (a)  $Br_2/hv$ , alc. KOH

(b) Br<sub>2</sub>/hv, aq. KOH

(c)  $Br_2/CCl_4$ , LiAlH<sub>4</sub>

- (d) Br<sub>2</sub>/CCl<sub>4</sub>, NaBH<sub>4</sub>
- **B.** Conversion  $R CH_2 OH \longrightarrow R CHO$  can be done by:
  - (a) PCC/CH<sub>2</sub>Cl<sub>2</sub>

(b) Cu, 300°C

(c)  $CrO_3$ 

- (d) All of these
- **C.** Conversion  $R CHO \longrightarrow R CO_2H$  can be done by:
  - (a) KMnO<sub>4</sub>

(b) H<sub>2</sub>CrO<sub>4</sub>

(c) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

- (d) All of these
- **D.** Conversion  $R CO_2H \longrightarrow R CHO$  can be done by:
  - (a) LiAlH<sub>4</sub>

(b) NaBH<sub>4</sub>

(c) DIBAL - H

- (d) All of these
- **E.** Conversion R CHO  $\longrightarrow R$  CH<sub>2</sub> OH can be done by:
  - (a) LiAlH<sub>4</sub>

(b) NaBH<sub>4</sub>

(c) H<sub>2</sub>/Ni

- (d) All of these
- **F.** Reduction  $R CH_2 OH \longrightarrow R CH_3$  can be done by:
  - (a) LiAlH<sub>4</sub>

(b) NaBH<sub>4</sub> - AlCl<sub>3</sub>

(c) H<sub>2</sub> - Ni

(d) Red P + HI

## 4. Which of the following is true for 3-methylbutanal?

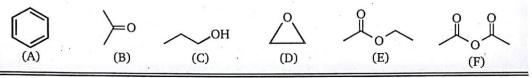
a.	This compound may be classified as an aldehyde.				
ь.	This compound may be classified as a ketone				
c.	An aldol reaction takes place on treatment with NaOH solution.				
d.	There is no reaction with LiAlH <sub>4</sub> in ether solution.				
e.	An excess of CH <sub>3</sub> MgBr in ether reacts to give 4-methyl-2-pentanol.				
f.	Wolff-Kishner reduction gives butane.				
g.	This compound is an isomer of 3-pentanone.				

5. This problem is an introduction to the planning of multistep syntheses.

For use, you have six reactant compounds ( $\bf A$  through  $\bf F$ ); and eight reagents ( $\bf 1$  through  $\bf 8$ ), shown below.

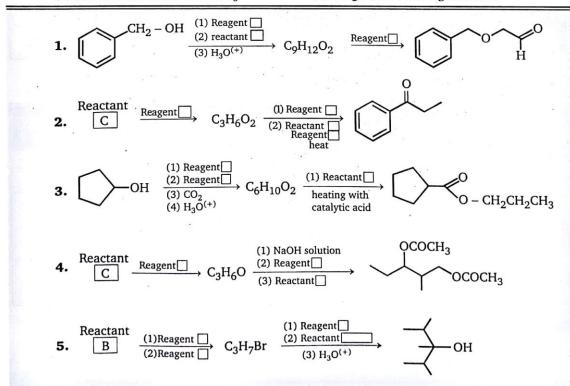
Following these lists, five multistep syntheses are outlined. For each of these, certain reactants or reagents must be identified by writing an appropriate letter or number in designated answer boxes. Write a single letter or number, indicating your choice of the best reactant or reagent, in each answer box.

## **Reactant Compounds:**



#### Reagents:

- (1) Jones' reagent [Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in H<sub>3</sub>O<sup>+</sup>]
- (3) Sodium hydride NaH
- (5) Thionyl chloride SOCl<sub>2</sub>
- (7) Aluminium trichloride AlCl<sub>3</sub>
- (2) PCC [CrO<sub>3</sub> in pyridine + HCl]
- (4) Sodium borohydride NaBH<sub>4</sub>
- (6) Phosphorus tribromide PBr<sub>3</sub>
- (8) Magnesium turnings in ether



6. Which of the following is true for 3-methyl-2-butanone?

a.	It may be prepared by CrO <sub>3</sub> oxidation of 2-methyl-2-butanol.					
ь.	Its reaction with NaBH <sub>4</sub> gives a secondary alcohol.					
c.	It may be prepared by acidic Hg 2+ catalyzed hydration of 3-methyl-1-butyne.					
d.	It forms a silver mirror on treatment with [Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> .					
e.	This compound is an isomer of 4-penten-1-ol.					

7. Which of these methods would serve to prepare 1-phenyl-2-propanol?

a.	Addition of benzyl Grignard reagent to acetaldehyde (ethanal).					
ъ.	Addition of phenyl lithium to propylene oxide (methyloxirane).					
c.	Addition of phenyl Grignard reagent to acetone (2-propanone).					
d.	Acid-catalyzed hydration (addition of water to) of 2-phenyl-1-propene.					
e.	Addition of methyl Grignard reagent to acetophenone (methyl phenyl ketone).					
f.	Addition of methyl Grignard reagent to phenylacetaldehyde.					

## 8. Match the Column (I) and (II).

	Column (I)	Column (II)			
	Reaction	ā	Name of Reaction		
(a)	$\begin{array}{c c} OH & OH \\ \hline & & \\ \hline & & \\ \hline \end{array} \xrightarrow{V}$	(p)	Pinacol-Pinacolone rearrangement		

## ALCOHOL, ETHERS AND EPOXIDES

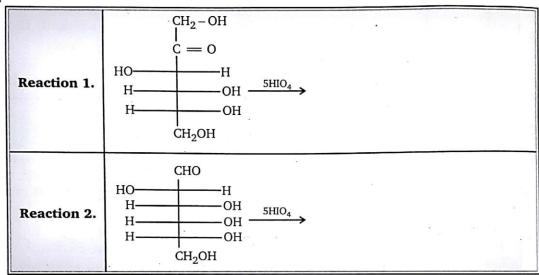
385

(b)	$\begin{array}{c c} & & & \\ \hline \\ \hline$	(q)	Semi-Pinacol reaction
(c)	$\begin{array}{c} & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$	(r)	Pinacolic-Diazotization
(d)	$\begin{array}{c c} & & & & \\ \hline & & & & \\ \hline & & & & \\ \hline & & & &$	(s)	Pinacol fashion reaction

## 9. Match the Column (I) and (II).

	Column (I)		Column (II)
	Reactant		Products
(a)	$ \begin{array}{c} \text{CH}_{3} \\ \text{OH} \end{array} \xrightarrow{\text{CH}_{3}\text{OH}} \xrightarrow{\text{H}_{2}\text{SO}_{4}\text{ Conc.}} $	(p)	CH <sub>3</sub> 14 OCH <sub>3</sub>
(ь)	$ \overset{CH_3}{\overset{*}{OH}} \xrightarrow{(1)NaH}  $	(q)	CH <sub>3</sub>
(c)	$ \overset{CH_{3}}{\overset{(1) \text{ HBr}}{\overset{(2) \text{ Mg}}{\overset{(3) \text{ CH}_{3} \text{I}}}}} $	(r)	OČH <sub>3</sub>
(d)	$ \begin{array}{c} CH_3 \xrightarrow{(1) \text{Na}} \\ OH \xrightarrow{(2) \text{CH}_3 \text{I}} \end{array} $	(s)	OCH <sub>3</sub>

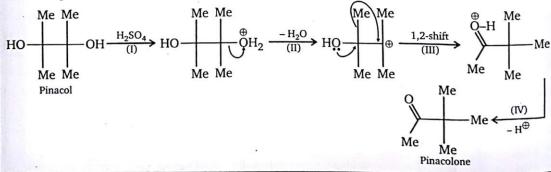
10.



Ratio of moles of formaldehyde obtained in the reaction (1) and reaction (2)?

## 11. Comprehension

Di-tert-glycols rearrange in the presence of acid to give  $\alpha$ -tertiary ketones. The trivial name of the simplest glycol of this type is pinacol, and this type of reaction therefore is named pinacol rearrangement (in this specific case, the reaction is called a pinacol-pinacolone rearrangement). The rearrangement involves 4 steps. one of the hydroxyl groups is protonated in the first step. A molecule of water is eliminated in the second step and a tertiary carbocation is formed. The carbocation rearranges in the third step into a more stable carboxonium ion via a [1, 2] rearrangement. In the last step, the carboxonium ion is deprotonated and the product ketone is obtained.



A. What is R.D.S. of pinacol-pinacolone rearrangement?

(a) I step

(b) II step

(c) III step

(d) IV step

B. 
$$HO \xrightarrow{\text{Et Ph}} OH + HO \xrightarrow{\text{CH}_3 \text{Ph}} OH \xrightarrow{\text{H}_2 \text{SO}_4} \rightarrow$$

How many products obtained in above reaction?

(a) 1

(b) 2

(c) 3

(d) 4

C. 
$$CH_2-Cl \xrightarrow{AgNO_3} P$$

Product 'P' is:

**D.** 
$$CH_3 \xrightarrow{CH_3 CH_3} CH_3 \xrightarrow{NaNO_2} (A)$$
  
 $OH NH_2$ 

Product (A) is:

(a) 
$$CH_3 - C - C - CH_3$$
  
 $CH_3 - CH_3$ 

(b) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

(d) None of these

## **SUBJECTIVE PROBLEMS**

1. 
$$(A)$$
  $\xrightarrow{\text{4 moles of PCC}}$   $CH = 0$   $CH = 0$ 

Maximum number of moles of Ac2O consumed by reactant (A) is:

#### **ANSWERS — LEVEL 2**

- 1. I B; II A; III A; IV B; V B
- 2. A-d; B-a, c, e, f, g, h; C-a, b, c; D-d; E-d, e, f, g, h; F-e
- 3. A-b; B-d, C-d, D-c, E-d; F-d
- 4. a, c, e, g

5. 
$$CH_2 - OH \xrightarrow{\text{(1) Reagent 3}} \text{(2) reactant d} \xrightarrow{\text{(2) reactant d}} C_9H_{12}O_2 \xrightarrow{\text{Reagent 2}} OH$$

$$\begin{array}{c|c} \text{Reactant} & \xrightarrow{\text{Reagent2}} & \text{C}_3\text{H}_6\text{O} & \xrightarrow{(1) \text{ NaOH solution}} & \text{OCOCH}_3 \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & & \\ \hline \text{C} & & & & & & & & \\ \hline \text{C} & & & & & & & & \\ \hline \text{C} & & & & & & & & \\ \hline \text{C} & & & & & & & & \\ \hline \text{C} & & & & & & & & \\ \hline \text{C} & & & & & & & \\ \hline \text{C} & & & & & & & \\ \hline \text{C} & & & & & & & \\ \hline \text{C} & & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & & & \\ \hline \text{C} & & & & \\ \hline \text{C} & &$$

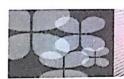
Reactant (1) Reagent (2) Reagent (2) Reactant (2) Reactant (3) 
$$H_3O^{(+)}$$
 OH

- **6.** b, c, e
- 8. a p, b r, c s, d q
- 10. Ratio of reaction I and II = 2
- 7. a, b, f
- 9. a-s, b-r, c-q, d-p
- 11. A-b; B-b; C-c; D-a

#### **Subjective Problems**

1. 4

## **ALDEHYDES AND KETONES**



# LEVEL- ]

1. 
$$\bigcap_{NO_2}^{O}$$

 $\xrightarrow{N_2H_4/KOH/H_2O}$ (Wolff-Kishner reduction)

(A); Product A is:

(b) 
$$OO_2$$
  $OH$   $OO_2$   $OH$   $OO_2$   $OOO_2$ 

2. 
$$\bigcirc C - CH_3 \longrightarrow \bigcirc CH_2 - CH_3$$

$$CH_2 - CH_2 - NMe_3 \longrightarrow \bigcirc CH_2 - CH_2 - NMe_3$$

Above conversion can be achieved by:

- (a) Wolf-Kishner reduction.
- (b) Clemmensen reduction

(c) LiAlH<sub>4</sub>

(d) NaBH<sub>4</sub>

3. 
$$CH_3 - C - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 - (CH_2)_3 - CH - CH_2$$

Above conversion can be achieved by:

- (a) Wolff-Kishner reduction
- (b) Clemmensen reduction
- (c)  $HS CH_2 CH_2 SH$ , following by Raney Ni
- (d) None of these

4. 
$$C \to CH_3$$
 $C \to CH_3$ 
 $C \to CH_2$ 
 $C \to CH_3$ 
 $C$ 

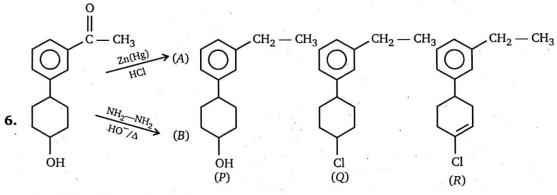
5. 
$$CH_3 - CH - CH_2 - CH_2 - CH_3 - CH_3 - CH - (CH_2)_3 - CH_3$$

Above conversion can be achieved by:

- (a) Wolff-Kishner reduction
- (b) Clemmensen reduction

(c) LiAlH<sub>4</sub>

(d) NaBH<sub>4</sub>



Identify product (A) & (B) from the given product P,Q,R:

(a) 
$$A = P, B = Q$$

(b) 
$$A = Q, B = R$$

(c) 
$$A = Q$$
,  $B = P$ 

(d) 
$$A = R, B = P$$

7. 
$$C - CH_3$$
 $C - CH_3$ 
 $C - CH$ 

(a) 
$$HO$$
  $CH_2-CH_3$ 

(c)

8. 
$$\frac{N_2H_4}{HO^-, \Delta}$$
 (A); Product (A) is:
$$CH_2 - CH_2 - Br$$

9.

Above conversion can be carried out by:

- (a) Clemmensen reduction
- (b) Wolff-Kishner reduction

(c) LiAlH<sub>4</sub>

- (d) NaBH<sub>4</sub>
- 10. Increasing order of equilibrium constants for the formation of a hydrate:

(a) IV < III < II < I

(b) IV < III < I < II

(c) I < II < III < IV

(d) II < III < I < IV

11. 
$$\bigcirc$$
 C=C  $\bigcirc$  OCH<sub>3</sub>  $\xrightarrow{\text{HgSO}_4}$   $\xrightarrow{\text{Major product}}$  Product (A) is:

12. 
$$0 \longrightarrow 0 \longrightarrow (A)$$

$$Me \quad Me$$

Predict the product of hydrolysis of the above molecule.

(a) 
$$CH_3$$

$$\overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longrightarrow}$$

- (a)  $Me_2CO/H^+$ ,  $H_3O^{\oplus}$ ,  $KMnO_4/HO^{-}$
- (c) KMnO<sub>4</sub>/NaO<sub>4</sub>, Me<sub>2</sub>CO/H<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>

- (b) CO<sub>2</sub>H
- (d) O CO<sub>2</sub>H
- , This conversion can be achieved by :
  - (b)  $Me_2CO/H^+$ ,  $KMnO_4$ ,  $H_3O^+$
  - (d)  $KMnO_4/NaIO_4$ ,  $H_3O^+$ ,  $Me_2CO/H^+$
- 14.  $H_3O^{\oplus} \rightarrow A + B$ . Compound (A) & (B) can be differentiated by:
  - (a) 2-4-DNP

13.

(c) Lucas reagent

- (b) Fehling solution
- (d) NaHSO<sub>3</sub>

Reagents to carry out above conversion, P, Q, R respectively are:

(a) 
$$H_2C = CH - CH_2 - Br$$
,  $(HO^{\Theta})$ ,  $[HO^{\Theta}, \Delta]$ , Wacker-process

(b) 
$$H_2C = CH - CH_2 - Br(HO^{\Theta})$$
, Wacker-process,  $HO^{\Theta}$ ,  $\Delta$ 

(c) Wacker process, 
$$H_2C = CH - CH_2 - Br(HO^{\Theta})$$
,  $HO^{\Theta}(\Delta)$ 

(d) Wacker process, 
$$HO^{\Theta}(\Delta)$$
,  $H_2C = CH - CH_2 - Br(HO^{\Theta})$ 

Above reaction is a Baeyer Villiger rearrangement of an asymmetric ketone with magnesium mono peroxo pthalate hexahydrate (in the drawing, Mg<sup>+2</sup> is omitted for clearity) Identify major product.

(a) 
$$\bigcap_{R}$$
 (b)  $\bigcap_{R}$  (c)  $\bigcap_{R}$  (d)  $\bigcap_{R}$  18.  $\bigcap_{R}$  OCH<sub>3</sub> and  $\bigcap_{R}$  OH,

Above compounds can be differentiated by following reagent:

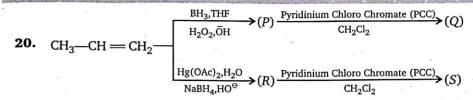
- (a) 2-4 DNP (Brady reagent)
- (b) Tollen's reagent

(c) Lucas reagent

(d) NaHSO<sub>3</sub>

19. 
$$OH \xrightarrow{\text{OC (excess)}} (A) \xrightarrow{\text{I equivalent}} (B) \xrightarrow{\text{CH}_3\text{MgBr}} (C) \xrightarrow{\text{NaBH}_4} (D)$$

Product (D) will be:



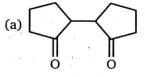
Relationship between products (Q) and (S) is:

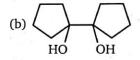
(a) Positional isomer

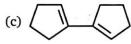
(b) Chain isomer

(c) Stereoisomer

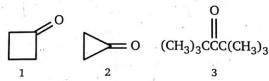
- (d) Functional isomer
- **21.** In the reaction,  $\underbrace{ O \xrightarrow{1.\text{Al(Hg), benzene, heat}}}_{O, \text{heat}} X, \text{ the product } (X) \text{ is :}$



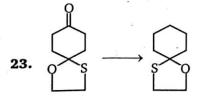




- (d)
- **22.** Rank the following in order of increasing value of the equilibrium constant for hydration,  $K_{\mathrm{hyd.}}$  (smallest value first).



- (a) 1 < 2 < 3
- (b) 3 < 1 < 2
- (c) 2 < 1 < 3
- (d) 2 < 3 < 1



Above conversion can be achieved by:

(a) Zn(Hg), HCl

(b)  $NH_2 - NH_2/KOH/\Delta$ 

(c) LiAlH<sub>4</sub>

(d) H<sub>2</sub>/Ni

3. PCC, CH<sub>2</sub>Cl<sub>2</sub>

24. Which sequence represents the best synthesis of hexanal?

3. 
$$\rm H_3O^+$$
  
4. PCC,  $\rm CH_2Cl_2$ 

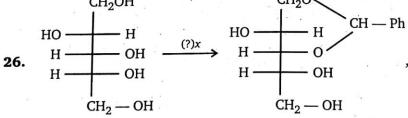
3. LiAlH<sub>4</sub>

(c) 
$$1. \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}$$
 (d)  $1. \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{MgBr} + \text{H}_{2}\text{C} - \text{CH}_{2}$ 

2. H<sub>3</sub>O<sup>+</sup>

25. (A) (A) (B), Product (B) in this reaction is :

(a) (C) (C)



Compound (x) in the above reaction is:

(a) 
$$Ph - C - CH_3$$
 (b)  $Ph - C - H$  (c)  $Ph - CH_2 - C - H$  (d)  $Ph - CH_2 - C - CH$ 

Product (C) of the above reaction is:

(a) 
$$^{\circ}$$
 Ph —  $^{\circ}$  CO<sub>2</sub>H

(a) 
$$Ph - CH_2 - NO_2$$

(b) 
$$Ph - CH_2 - ONO$$

(d) 
$$Ph - O - N = O$$

Product (A) of the above reaction is (bromination occur not in the benzene ring):

Вr

30. 
$$C_6H_{12}O_3$$
 Tollens test  $H_2O$  drop of  $H_2SO_4$ 

Compound (A) is:

(a) 
$$CH_3 - C - CH - CH_2$$
  
 $OCH_3 OCH_3$ 

(b) 
$$CH_3 - C - C - CH_3$$
  
| | | OCH<sub>3</sub>

Positive Tollens test

(c) 
$$CH_3 - C - CH_2 - CH - OCH_3$$
 (d)  $H - C - CH_2 - CH_2 - CH - OCH_3$  OCH<sub>3</sub>

31. 
$$C_{16}H_{16} \xrightarrow{O_3} (B) \xrightarrow{NH_2-NH_2} ;$$
 Reactant (A) in this reaction is :

(a) 
$$Ph$$
  $C = C < CH_3$   $CH_3$   $Ph$   $Ph$ 

(c) 
$$\frac{Ph}{CH_3}C = C \frac{Ph}{CH_3}$$

(b) 
$$CH_3$$
  $C = C < CH_3$   $Ph$ 

(d) both (b) and (c)

Compound (P) is:

(a) 
$$\mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_3}$$
 OH

O OH 
$$|| & | \\ || & | \\ \text{(b) CH}_3 - \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$$

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

33. Correct order of reactivity of following compounds towards Grignard reagent?

$$CH_3$$
— $C$ — $C$ 

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

34. 
$$CH_3$$
 —  $CH$  —  $CH$  —  $CH$  —  $CH_2$  —  $OH$  —

(a) 
$$CH_3$$
  $O$   $O$ 

$$(b) \xrightarrow{CH_3} O \xrightarrow{CH_2 - Ph}$$

$$CH_3$$
 $CH - Ph$ 
 $CO O O$ 

35. 
$$(CH_3)_3CO - CH_2 - CH_2 - CH_2 - CH_3 - CH_3$$

Total number of products obtained in above reaction is :

(a) 2

(b) 3

(c) 4

(d) 5

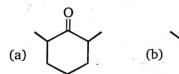
**36.** What reagent and/or reaction conditions would you choose to bring about the following conversion?

(a) 1. LiAlH<sub>4</sub>, 2. H<sub>2</sub>O

(b) H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, heat

(c) H<sub>2</sub>O, NaOH, heat

- (d) PCC, CH<sub>2</sub>Cl<sub>2</sub>
- 37.  $\stackrel{\text{Mel excess}}{\longrightarrow} 81\%$  yield; Product of the reaction is:





The above reduction can be best carried out by:

- (a) Clemmensen reduction
- (b) Wolff-Kishner reduction

(c) NaBH<sub>4</sub>

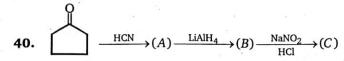
(d) None of these

**39.** 
$$CH_3 - C \equiv CH \xrightarrow{HgSO_4 \text{dil. } H_2SO_4} (A)$$

$$CH_3 - C \equiv CH \xrightarrow{(1)BH_3 \cdot THF} (B)$$

Product (A) and (B) is differentiated by:

- (a) 2-4-DNP
- (b) NaOI
- (c) Na-metal
- (d) NaHSO<sub>3</sub>

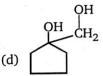


End product (C) in above reaction is:





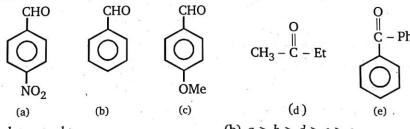




- Compound (X) C<sub>4</sub>H<sub>8</sub>O, which reacts with 2, 4-DNP derivative and gives negative haloform 41. test is:



- When a nucleophile encounters a ketone, the site of attack is: 42.
  - (a) the carbon atom of the carbonyl
  - (b) the oxygen atom of the carbonyl
  - (c) both the carbon and oxygen atoms, with equal probability
  - (d) no attack occurs as ketones do not react with nucleophiles
- The correct order of rate of reaction toward nucleophilic addition reaction: 43.



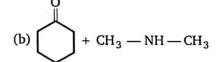
(a) a > b > c > d > e

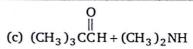
(b) a > b > d > c > e

(c) a > d > e > b > c

- (d) a > b > e > d > c
- OH would be best classified as a(an):
  - (a) Acetal
- (b) Hemiacetal
- (c) Hydrate
- (d) Cyanohydrin
- Which of the following pairs of reactants is most effective in forming an enamine? 45.

O 
$$\parallel$$
 (a)  $CH_3CH_2CH + [(CH_3)_2CH]_2NH$ 





- (d) None of these form an enamine.
- **46.** The reaction of  $C_6H_5CH = CHCHO$  with LiAlH<sub>4</sub> gives :
  - (a) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH

(b)  $C_6H_5CH = CHCH_2OH$ 

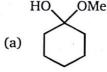
(c) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CHO

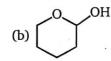
- (d) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHOHCH<sub>3</sub>
- 47.  $(A) \xrightarrow{\text{NaBH}_4} (A) \xrightarrow{\text{H}^+} (B)$ ; Product (B) of the reaction is:



- (b) O
- (c) 0
- (d) OI

48. Which of following compound is hemiacetal?







- (d) all of these
- **49.** Ph—CH<sub>2</sub>—C  $\equiv$  N  $\xrightarrow{\text{LDA}}$   $\xrightarrow{\text{CH}_3\text{I}}$  71%; End product of the reaction will be:
  - (a)  $Ph CH_2 CH_2 NH_2$
- (b)  $Ph CH_2 NH_2$

(c)  $Ph - CH - C \equiv N$  $CH_3$ 

- (d)  $Ph CH = C = N CH_3$
- 50.  $Ph CH = CH C CH_3 \longrightarrow Ph CH = CH CO_2H$

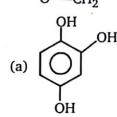
Above conversion can be achieved by:

- (a) KMnO<sub>4</sub>, ∆ followed by H<sup>+</sup>
- (b) I<sub>2</sub>/NaOH followed by H<sup>+</sup>

(c)  $H_2/Pt$ 

(d) LiAlH<sub>4</sub>

- 51.
- $H_3O^{\oplus}$  Products; Product of the reaction is/are:



- (p) OH OH
- (c) HCHO
- (d) Both (a) and (c)

**52.**  $SeO_2 \rightarrow (A)$ ; Product (A) of the reaction is :

53.  $CH_3 \xrightarrow{CH_3} \xrightarrow{Br_2+NaOH} \xrightarrow{\Delta} (A) + CHBr_3$ ; Product (C) of the reaction is:

Product (A) of the reaction will be:

(a) 
$$CH_3 - CH_2 - C - CH_2 - C - CH_2 - CH_3$$

(b) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

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

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

**55.**  $R - C - H \xrightarrow{R-NH_2} R - CH = N - R$ . This reaction gives best yield at :

- (a) pH 1 2
- (b) pH 4 5
- (c) pH 10 11
- (d) pH 13 14

An aromatic compound A of the molecular formula  $C_8H_{10}O$  on reaction with iodine and dilute NaOH gives a yellow precipitate. The structure of the compound is expected to be:

(b) C<sub>6</sub>H<sub>5</sub>CHOHCH<sub>3</sub>

(c) 
$$CH_3 - CH_2OH$$

(d) CH<sub>3</sub>—OH

- 57. Compound A (molecular formula C<sub>3</sub>H<sub>8</sub>O) is treated with acidified potassium dichromate to form a product B(molecular formula C<sub>3</sub>H<sub>6</sub>O). B forms a shining silver mirror on warming with ammonical silver nitrate, B when treated with an aqueous solution of  $NH_2NHCONH_2$ and sodium acetate gives a product C. Identify the structure of C.
  - (a)  $CH_3CH_2CH = NNHCONH_2$
- (b)  $CH_3C = NHHCONH_2$ CH<sub>3</sub>
- (c)  $CH_3C = NCONHNH_2$
- (d)  $CH_3CH_2CH = NCONHNH_2$
- In the reaction, the acid obtained will be :  $CH_3CH(OH)CN \xrightarrow{H-OH} CH_3CH(OH)COOH$ **58.** 
  - (a) D-isomer

(b) L-isomer

(c) (80%D + 20%L) mixture

- (d) (50%D + 50%L) mixture
- 59. In the following sequence:

NaCN acetic anhydride → (iii), Product (iii) is: CH3CH2Cl-

(a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

- (b) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CONHCH<sub>3</sub>
- (c) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NHCOCH<sub>3</sub>
- (d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CONHCOCH<sub>3</sub>
- KMnO<sub>4</sub> 60. H<sub>2</sub>O, Δ

Product (G) is:

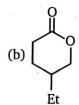
(a) 
$$C - OH$$

(b) 
$$HO - CH_2$$
  $CO_2H$ 

- Carbonyl compounds can generally be converted to hydrocarbons by: 61.
  - (a) H<sub>2</sub>/Pt
- (b) LiAlH<sub>4</sub>
- (c)  $N_2H_4$ -KOH/ $\Delta$
- (d) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> H<sub>2</sub>SO<sub>4</sub>

 $(1) O_3$ 62.  $\rightarrow$  (A); Product (A) is: (2) Ag<sub>2</sub>O (3) NaBH<sub>4</sub> (4) H<sup>⊕</sup>









- 63. Which statement about the aldol condensation is correct?
  - (a) A Lewis acid is commonly used as a catalyst
  - (b) The initial step is probably the formation of a carbanion
  - (c) A Lewis base is employed to induce carbocation formation
  - (d) The carbon chain is lengthened through the elimination of 1 mole of water
- **64.** A compound gives a positive test with  $I_2/NaOH$  and is extracted from benzene by saturated NaHSO $_3$ . It may be :
  - (a) CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CHO

(b)  $CH_3(CH_2)_3COCH_3$ 

(c) CH<sub>3</sub>CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub>

- (d) CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>OH
- **65.** Which of the following compounds on reaction with excess CH<sub>3</sub>MgBr and subsequent hydrolysis will give a tertiary alcohol?
  - (a) C<sub>2</sub>H<sub>5</sub>CHO
- (b) C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>CH<sub>3</sub>
- (c) C<sub>2</sub>H<sub>5</sub>COOH
- (d) CH<sub>3</sub>CH—CHCH<sub>3</sub>

$$66. \quad A+B \longrightarrow \bigcirc$$

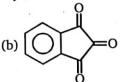
Reactant (A) and (B) is:

- (a) Ph— $CH_2$ — $CH = O + NH_2$ —OH
- (c) Ph—C—CH<sub>3</sub> + NH<sub>2</sub>—NH<sub>2</sub>
- (b) Ph— $CH = O + NH_2$ —OH
- || (d) Ph—C—CH<sub>3</sub> + NH<sub>2</sub>—OH
- 67.  $CH_3 C OH \xrightarrow{Ca(OH)_2} (A)$

Product (A) is:

- (a) //C
- OH OH

- (b) (c)
- (d) OH
- **68.** Which of the following does not form a stable hydrate on addition of H<sub>2</sub>O?
  - (a) Ph C C C Ph







69. Consider the following sequence of reactions.

00/00/00/00/00/00/

Ketone 
$$A \xrightarrow{1. C_2H_5MgBr} B \xrightarrow{H_2SO_4, \text{ heat } \atop -H_2O} C \xrightarrow{1. O_3} + H_2O$$
The ketone (A) is:

**70.** In the reaction,

$$(a) \begin{array}{c} + \text{ CH}_3\text{COCH}_3 & \xrightarrow{\text{EtONa/EtOH}} X, \text{ the product } (X) \text{ is :} \\ H_3\text{C} & \text{CH}_3 \\ \text{(b)} & \text{OH} \\ \end{array}$$

$$(b) \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array}$$

- **71.** The conversion of acetophenone into benzoic acid can be achieved by its reaction with:
  - (a) sodium hydroxide followed by acidification
  - (b) iodine and sodium hydroxide, followed by acidification
  - (c) hydroxylamine followed by reaction with H2SO4
  - (d) m-chloroperoxobenzoic acid
- 72. In which of the following compounds the methylenic hydrogens are the most acidic?
  - (a) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>

- (b) CH<sub>3</sub>CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>
- (c) CH<sub>3</sub>CH<sub>2</sub>CH(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>
- (d) CH<sub>3</sub>COCH<sub>2</sub>CN
- **73.** Which is the major product of the following reaction?

$$(a) \qquad \stackrel{\text{NH}_2\text{OH}}{\longleftarrow} O \qquad \stackrel{\text{NH}_2\text{OH}}{\longleftarrow} O \\ \text{NHOH} \qquad (b) \qquad O \\ \text{ONH}_2 \qquad (c) \qquad O \\ \text{OH} \qquad (d) \qquad$$

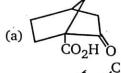
74. Ph—C—OH 
$$\xrightarrow{\text{SOCl}_2}$$
 (A)  $\xrightarrow{\text{H}_2}$  (B)

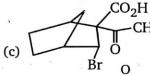
Product (B) is:



(d) 
$$Ph$$
— $CH = CH_2$ 

- 75. The presence of unsaturation in organic compounds can be tested with:
  - (a) Schiff's reagent
- (b) Tollens' reagent (c) Fehling's reagent (d) Baeyer's reagent
- 76. Which of the following gives iodoform test?
  - (a) CH<sub>3</sub>CH<sub>2</sub>OH
- (b) C<sub>2</sub>H<sub>5</sub>CHO
- (c)  $(CH_2OH)_2$
- (d) None of these
- Which of the following  $\beta$ -keto carboxylic acid does not undergo decarboxylation on heating? 77.





- (d) None of these
- OCH<sub>2</sub>CH<sub>3</sub> PCC  $H_2C = CHMgBr$ HOCH2CH2CH2 (1 molar equivalent)

$$\xrightarrow{\text{KOH}} \xrightarrow{\text{H}_3\text{O}^{\oplus}} \xrightarrow{\text{(CH}_3 - \text{C)}_2\text{O}} \xrightarrow{\text{Pyridine}} (D)$$

Product (D) is:

(b) 
$$H_2C = CH - CH_2 - C - CO_2H$$

(c) 
$$H_2C = CH - C - CH_2 - CH_2 - CH_2 - C - CH_3$$
  
OH

(d) 
$$H_2C = CH - CH_2 - CH - CH_2 - C - O - H$$
  
OH

79. The compound shown in the below undergoes racemization on reaction with aqueous acid.

Which of the following structures best represents the intermediate responsible for this process?

**80.** The final product of the following sequence of reaction is :

**81.** The amino ketone shown below undergoes a spontaneous cyclization on standing. What is the major product of this intramolecular reaction?

$$CCH_{3}$$

$$CH_{2}CHNH_{2}$$

$$CH_{3}$$

**82.** Compound (A)  $C_6H_{12}O$  is optically active. Compound (A) give negative Tollens test and positive test with 2-4-di-nitro phenyl hydrazine. Identify A.

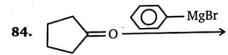
(a) 
$$CH_3 - CH_2 - CH_3 - CH_3$$

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

(d) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

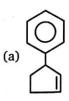
 $(1)\text{Et}_2\text{O} \rightarrow (A); \text{ Product } (A) \text{ of the reaction is :}$ 

$$(d) \bigcup_{\text{NO}_2}$$

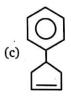


$$(N) \xrightarrow{\text{NH}_4\text{Cl}} (O) \xrightarrow{\text{HCl (conc.)}} (P) \xrightarrow{\text{KOH (4 molar)}} (Q)$$

Product (Q) will be:



(b)





**85.** 
$$Ph \longrightarrow CH_3 \xrightarrow{CrO_2Cl_2} (A) \xrightarrow{conc.KOH} Ph \longrightarrow CH_2OH + (B)$$

Product (B) of above the reaction is:

(a) 
$$Ph - CO_2H$$

(b) 
$$Ph - CO_2$$

(d) 
$$Ph - CH_3$$

86.  $H \xrightarrow{CHO} OH \xrightarrow{(i)KCN} Product$ ; Product obtained in the reaction is:

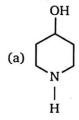
CH<sub>2</sub> — OH D-(+)-Glyceraldehyde

(a) Diastereomer

(b) Racemic

(c) Meso

- (d) Optically pure enantiomer
- 87.  $NH_2OH \rightarrow (A) \xrightarrow{H^+} (B) \xrightarrow{LAH} (C)$ ; Product (C) of the reaction is :



Product (A) and (C) is:

(a) 
$$\longrightarrow$$
 CH<sub>3</sub>; CHI<sub>3</sub>

(b) 
$$\begin{bmatrix} O \\ \parallel \\ C - CH_3 \end{bmatrix}$$
 CHI<sub>3</sub>

(c) 
$$\longrightarrow$$
 CH<sub>14</sub> CH<sub>3</sub>; CHI<sub>3</sub>

(d) 
$$\bigcirc$$
 CH<sub>2</sub>—CHO; CHI<sub>3</sub>

89. Ph—CH—CH<sub>3</sub> 
$$\xrightarrow{\text{PCC}}$$
 (A)  $\xrightarrow{\text{NH}_2-\text{NH}-\text{C}-\text{NH}_2}$  (B)

Product (B) is:

(b) 
$$Ph$$
— $C = N$ — $NH$ — $C$ — $NH_2$ 
 $CH_3$ 

(c) 
$$Ph$$
— $CH = N$ — $N$ — $C$ — $NH_2$   $CH_3$ 

(d) 
$$Ph$$
— $CH = N$ — $C$ — $NH2$ 

90. 
$$\underbrace{\begin{array}{c} O \\ \\ \end{array}}_{\text{H}^{\oplus}} (P)$$

Product (P) is:

- (a) Hemiacetal
- (b) Acetal
- (c) Alcohol
- (d) Alkane

$$(d) \bigcirc CH_2$$
 
$$OMe$$

Reactant	K <sub>eq</sub> .
PhCHO	а
Ů	10 1 - <b>b</b>
O    Ph — C— CH <sub>3</sub>	с
O	d

The correct order of decreasing value of  $K_{\rm eq.}$  is :

(a) a > b > c > d

(b) d > a > b > c

(c) d > b > a > c

(d) d > a > c > d

93. Product (B) of the given reaction is:

ατού, αλαπού

$$(a) \qquad \begin{array}{c} & & & \\ & &$$

**94.** End product (*C*) of the reaction is :

95. (A) O<sub>3</sub> does not undergo self aldol condensation  $C_{11}H_8O \xrightarrow{O_3} Ph - CHO + 2b \xrightarrow{Ag^+} oxalic acid$ 

Compound (A) will be:

(a) 
$$Ph - C \equiv C - C \equiv C - CHO$$

(b) 
$$Ph - C \equiv C - CH = CH - CHO$$

(c) 
$$Ph - CH = CH - C \equiv C - CHO$$

(d) 
$$Ph - CH = CH - C = CH - CO_2H$$

96. OH Product; Product of the reaction is:

Catalyst TsOH
0°C, 2h
(molecular sieves)



97. Which pair of reactants compounds may be used to make given acetal?

$$\begin{array}{c|c} & & \text{CH}_2-\text{OH} \\ & & \text{CH}_2-\text{OH} \\ & & \text{CH}_2-\text{OH} \end{array}$$

98. 
$$(A)$$
 CHO  $\xrightarrow{H^{\oplus}}$  (B); (A) & (B) are isomers; Isomer (B) is:

99. 
$$OH \xrightarrow{PCC} (A)$$

$$OH \xrightarrow{PCC} (B)$$

- (A) and (B) is differentiated by:
- (a) NaH
- (b) 2-4 DNA
- (c) Tollen's reagent (d) NaHSO<sub>3</sub>

100. Which of the following pairs cannot be differentiated by Tollens' reagent?

- (a) Benzaldehyde and benzyl alcohol
- (b) Hexanal and 2-hexanone
- (c) 2-Hexanol and 2-hexanone
- (d) Pentanal and diethyl ether

101. An optically active compound C<sub>6</sub>H<sub>12</sub>O gives positive test with 2, 4-dinitrophenyl hydrazine, but negative with Tollens' reagent, what is the structure of the compound?

(a) 
$$CH_3 - C - CH_2 - CH_2 - CH_2 - CH_3$$
 (b)  $H - C - CH - CH_2 - CH_2 - CH_3$   $CH_3$ 

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

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

**102.** Compound (A)  $C_6H_{12}O_3$ , when treated with  $I_2$  in aqueous sodium hydroxide gives yellow precipitate. When A is treated with Tollens reagent no reaction occur. When A is hydrolysed and then treated with Tollens reagent, a silver mirror is formed in test tube. Compound (A)

$$\begin{array}{c}
O \\
\parallel \\
(c) CH_3 - C - CH_2 - CH(OCH_3)
\end{array}$$

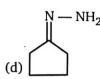
(d) 
$$H - C - CH_2 - CH_2 - CH(OCH_3)_2$$

**103.** 
$$CH_2 - CH_2 - CO_2H \xrightarrow{\Delta} A \xrightarrow{NH_2 - NH_2} B \xrightarrow{heat} (C)$$
, Product (C) obtained is:  $CH_2 - CH_2 - CO_2H$ 

(a) 
$$CH_3 - CH = CH - CH_2$$







**104.** Which of following does not react with NaHSO<sub>3</sub> (sodium bisulphite)?

(b) 
$$CH_3 - C - Et$$

(d) 
$$Ph - CH_2 - C - CH_3$$

$$105. \qquad \begin{array}{c} CH_2 - CH_2 - CH_2 - NH_2 \end{array}$$

 $\xrightarrow{\text{Raney Ni}} \text{H}_2 \rightarrow (A) \text{ ; Product } (A) \text{ is :}$ 

$$(d) \bigcirc \bigvee_{H}$$

106. 
$$+CH_2 = CH - CH_2 - Br \xrightarrow{KOH} (A)$$
; Product (A) is:

$$O \longrightarrow O - CH_2 - CH = CH_2$$

$$CH_2 - CH = CH_2$$
b) O

(c) 
$$CH_2 - CH = CH_2$$

$$(d) \bigcup_{\text{CH}_2-\text{CH}} \text{CH}_2$$

107. 
$$\frac{\text{(1)Me-Li(excess)}}{\text{(2)HCl/H}_2O} \rightarrow (A) \xrightarrow{\text{I}_2} \text{(B) + CHI}_3; \text{ Product (B) in this reaction is :}$$

Arrange the following reagent in the correct order in which above transformation is carried out:

- (a)  $KOD/D_2O$ ,  $H^+/\Delta$ , LiAlH<sub>4</sub>
- (b)  $H^+/\Delta$ , KOD/D<sub>2</sub>O, LiAlH<sub>4</sub>
- (c)  $KOD/D_2O$ ,  $LiAlH_4$ ,  $H^+/\Delta$
- (d) LiAlH<sub>4</sub>, H<sup>+</sup>/ $\Delta$ , KOD/D<sub>2</sub>O

109. 
$$CH_3 - C - H \xrightarrow{HCN} (A) \xrightarrow{H_3O^{\oplus}} (B) \xrightarrow{\Delta} (C) \xrightarrow{LiAlH_4} (D) \xrightarrow{HIO_4} HCHO + (E)$$

Compound (C)can show geometrical isomerism. Product (E) of the reaction will be:

(b) 
$$CH_3 - CH_2 - C - H$$

110. Arrange in their increasing order of equilibrium constants for hydration?

$$CH_3 - CH_3$$
,  $CH_3 - CH_3$ 

$$CH_3 - C - CH_2 - CI$$
,  $H - C - H$ 

$$Cl - CH_2 - C - H$$

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

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

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

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

111. End products of the following sequence of reactions are:

$$\begin{array}{c}
O \\
C - CH_3
\end{array}$$

$$\begin{array}{c}
-1.I_2 + \text{NaOH}, \Delta \\
2.H^+ \\
3.\Delta
\end{array}$$

112. Ph — CH<sub>2</sub> — CN 
$$\xrightarrow{\text{(1) EtONa}}$$
  $\xrightarrow{\text{(2) CH}_3 - \text{C} - \text{Cl}}$  (3)  $\text{H}_3\text{O}^{\oplus}/\Delta$  (P) ; Product (P) of the reaction will be :

(a) 
$$Ph - CH_2 - C - H$$

(c) 
$$Ph - CH - C - H$$

$$CH_3$$

(d) Ph — CH — C— CH
$$_3$$

113. 
$$C - H \xrightarrow{(i) \text{ NaCN} \atop (ii) \text{ H}_2 \text{SO}_4}$$
 Products. Products of the reaction are:

- (a) Racemic mixture
- (b) Diastereomers
- (c) Meso
- (d) Mixture of meso compound and optically active compound

114. (A) 
$$\xrightarrow{\text{HgSO}_4}$$
 (B)  $\xrightarrow{\text{LiAlH}_4}$  (C) recemic mixture

 $\therefore$  reactant (A) is:

(a)  $CH_3 - C \equiv CH$ 

(b)  $HC \equiv CH$ 

(c)  $CH_3 - C \equiv C - CH_3$ 

(d) Ph— $CH = CH_2$ 

115. 
$$CH_3CH_2 - C - CH_3 \xrightarrow{NaNO_2}$$
; Major product of this reaction is :

(b) 
$$CH_3 - CH_2 - C - CH = N - OH$$

(c) 
$$CH_3 - C - C - CH_3$$
 $\parallel$ 
 $N-OH$ 

(d) 
$$\operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{C} - \operatorname{CH}_3$$
  $\parallel$   $N$ — $\operatorname{OH}$ 

119. Cl 
$$\xrightarrow{\text{alc. KOH}}$$
 (A). Product (A) is:

120. 
$$R - C - R$$

$$(catalyst)$$
 $R - C - R$ 

$$(CATALYST)$$
 $R - C - R$ 

$$(CATALYST)$$

Which of following can be used as a catalyst in the above reaction?

(a) 
$$Cl^{-}$$
 (b)  $CH_3 - C - O^{-}$  (c)  $Et - O^{-}$  (d)  $HSO_4^{-}$ 

**121.** Arrange the following carbonyl compounds in decreasing order of their reactivity in nucleophilic addition reaciton.

(a) 
$$ii > iii > i > iv$$

(b) 
$$ii > i > iv > iii$$

(c) 
$$iii > ii > i > iv$$

(d) 
$$iii > i > iv > ii$$

**122.** The following reaction were carried out.

The final product formed in the above reaction sequence is:

(c) 
$$\stackrel{H}{\longrightarrow} O$$
  $\stackrel{O}{\longrightarrow} O$   $\stackrel{O}{\longrightarrow} O$ 

- **A.** Yield of each step as actually carried out in the laboratory is given above. What is overall yield of reaction?
  - (a) 42%

(b) 31%

(c) 21%

- (d) 60%
- **B.** What is the appropriate reagent to carry out above synthesis, i.e., A, B, C respectively are:
  - (a)  $Br_2/H^+$ , LiAlH<sub>4</sub>,  $H^{\oplus}$

(b)  $Br_2/H^+$ ,  $NaBH_4$ ,  $HO^-$ 

(c) NBS, AlCl<sub>3</sub>, HO

(d)  $Br_2/HO^-, BF_3, HO^-$ 

124. 
$$\bigcirc \bigcap_{\substack{\text{Ni} \\ \text{3H}_2 \\ \text{(High temp} \\ \& pressure)}} (A) \longrightarrow (B) \longrightarrow (B) \longrightarrow (C) \longrightarrow (D) \longrightarrow (E)$$

Product (E) is:

- (a) Nylon 66
- (b) Nylon 6
- (c) Styrene
- (d) Polystyrene
- 125. Methyl vinyl ketone on reaction with LiCuMe<sub>2</sub> gives a major product, whose structure is:

**126.** Which of following is in capable to show iodoform test?

$$H_2C = CH \xrightarrow{OH} CH_3$$

$$(d) \qquad H \qquad 0$$

$$CH_2 - C - CH$$

127. 
$$CH_3 - C - CH_2 - CH_2 - CH_3 \xrightarrow{O \ | \ (NH_4)_2 CO_3} (A) \xrightarrow{CCl_3 CO_2 Na} (B)$$
(major)

Product (B) of above reaction is:

(a) 
$$\bigcap_{N}^{Cl}$$
 (b)  $\bigcap_{N}^{Cl}$  (c)  $\bigcap_{N}^{Cl}$  (d)  $\bigcap_{N}^{Cl}$   $\bigcap_{Cl}^{Cl}$   $\bigcap_{N}^{Cl}$   $\bigcap_{N}^{Cl}$ 

128. EtO<sub>2</sub>C  $\xrightarrow{O}$   $\xrightarrow{A}$  ? Product obtained is :

(c) 
$$OH$$

129. (A)  $\xrightarrow{\text{LiAlH}_4}$  (B)  $\xrightarrow{\text{H}^{\oplus}}$  Diastereomers Ketone

Reactent (A) is:

(b) 
$$CH_3$$
— $C$ — $CH_2$ — $CH_3$ 

(d) 
$$CH_3$$
— $CH_2$ — $CH_2$ — $CH = O$ 

(d) None of these

130. 
$$4 \longrightarrow H_{30} \longrightarrow H_{30} \longrightarrow H_{4} \longrightarrow H_{30} \longrightarrow H_{4} \longrightarrow H_{30} \longrightarrow H_{4} \longrightarrow$$

Value of x in above reaction is:

131. 
$$(A) \xrightarrow{NH_2OH} (B) \xrightarrow{H_2SO_4} (C) \xrightarrow{H_3O^{\oplus}} (D) + (E) \xrightarrow{CHCl_3} CH_3 \longrightarrow CH_3 \longrightarrow$$

$$(D) \xrightarrow{\text{SOCl}_2} (F) \xrightarrow{\text{(i) PhMgBr(excess)}} (G) \xrightarrow{\text{H}^{\oplus}} (H) \xrightarrow{\text{CH}_2 I_2} Zn/\text{Cu}$$

Molecular weight of compound (A) is:

132. 
$$Ph_2CH - C - H \xrightarrow{\text{aqueous acid}} (A) + \text{enol} + \text{aldehyde}$$

$$\begin{array}{c} (A) + \text{enol} + \text{aldehyde} \\ 81\% & 2\% & 17\% \end{array}$$

Product (A) of above reaction will be:

(a) 
$$Ph - C = CH - O$$

$$Ph$$

$$\begin{array}{c} \text{Ph} \\ \text{OH} \\ | \\ \text{(c)} \ \text{Ph}_2 \text{CH} - \text{CH} - \text{OH} \end{array}$$

133. Which of the following will form stable hydrate?

(c) 
$$(CF_3)_2CO$$

134. The pH at which maximum hydrate is present in an solution of oxaloacetic acid:

$$H - O - C - C - CH_2 - C - O - H$$
  
 $pK_a = 2.2$   $pK_a = 3.98$ 

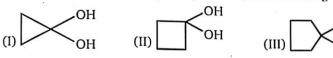
(a) 
$$pH = 0$$

(b) 
$$pH = 12$$

(c) 
$$pH = 4$$

(d) 
$$pH = 6$$

135. Arrange their stabilities of given gem-diols in decreasing order.



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

136. Maximum hydration takes place of:

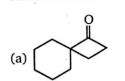
- 137. The conversion, PhCN  $\rightarrow$  PhCOCH<sub>3</sub>, can be achieved most conveniently by reaction with:
  - (a) CH<sub>3</sub>MgBr followed by hydrolysis
  - (b) I<sub>2</sub> NaOH, CH<sub>3</sub>I
  - (c) dil. H<sub>2</sub>SO<sub>4</sub> followed by reaction with CH<sub>2</sub>N<sub>2</sub>
  - (d) LAH followed by reaction with CH3I

138. 
$$\bigcirc \longrightarrow \bigcirc \longrightarrow \bigcirc \longrightarrow (A) \xrightarrow{\text{Zn(Hg)/HCl}} (B)$$

In the above reaction, product (B) is:

139. 
$$(A) \xrightarrow{\text{LiAlH}_4} (B) \xrightarrow{\text{H}^{\oplus}} \Delta$$

Structure of A is:



140. 
$$O \xrightarrow{O_3} HCHO + (A) \xrightarrow{Ph - NH_2} (B)$$

Product (B) is:

(a) 
$$Ph - NH - C - CO_2H$$

(b) 
$$Ph - NH - C - CH_2 - CO_2H$$

$$(d) O \longrightarrow N O$$

$$| Ph$$

To carry out above conversion, arrange the following reagents in correct order.

EtONa / EtOH/ $\Delta$ 

NaOCl

H<sup>+</sup> (4)

(a) 
$$1 \rightarrow 3 \rightarrow 2 \rightarrow 4$$

(b) 
$$1 \rightarrow 2 \rightarrow 4 \rightarrow 3$$

(c) 
$$1 \rightarrow 3 \rightarrow 4 \rightarrow 2$$

(d) 
$$1 \rightarrow 2 \rightarrow 3 \rightarrow 4$$

142. 
$$H_2C = CH - CH_2 - CH_2 - CH_3 - CH_3$$

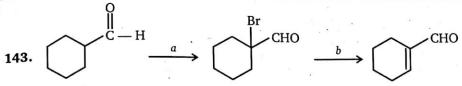
Product (B) is:

(a) 
$$H - C - CH_2 - CH_2 - CH_2 - CH_3$$

(b) 
$$H = C + CH_2 + CH_2 + C + C + C + CH_3$$

$$\begin{array}{c} \text{(c)} \ \ \text{H} - \text{O} - \overset{\text{C}}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{C}}{\text{C}} - \text{O} \\ \text{Et} \end{array} \\ \end{array} \\ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array}$$

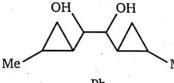
(d) 
$$H = C + CH_2 + CO + CH_3$$



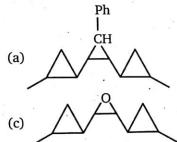
Identify appropriate reagents for the above reaction:

- (a)  $a = Br_2/CCl_4$ ,
- b = aq. KOH
- (b)  $a = Br_2/H^+$ ,
- b = aq. KOH
- (c)  $a = Br_2/H^+$ ,
- b = alc. KOH
- (d)  $a = Br_2/HO^-$ ,
- b = aq. KOH

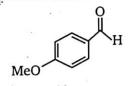
144.



 $\xrightarrow{\text{PhCHO}}$  (X); Product (X) of this reaction is:



- (b) CH
- (d) \_\_\_\_\_\_
- 145. The  $K_{eq.}$  values in HCN addition to following aldehydes are in the order :



- H
- Me<sub>2</sub>N H

- (a) I > II > III
- (II) (I
- (c) III > I > II
- (d) II > I > III

146.

(1)  $CH_3$ —C—CN  $K_1$  O +HCN  $CH_3$ 

(2) 
$$CH_3$$
— $C$ — $CN$   $K_2$   $O$ 
 $H$  +HCN

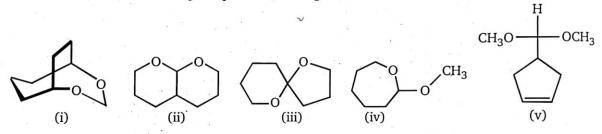
elation between  $K_1$  and  $K_2$  is:

- (a)  $K_1 = K_2$
- (b)  $K_1 > K_2$
- (c)  $K_2 > K_1$
- (d)  $K_1 = K_2 = 1$

147. Which of the following is correct for the reaction?

$$+ HCN \xrightarrow{pH=9 \text{ to} 10} (A)$$

- (a) A is cyanohydrin
- (b) Nucleophilic-addition reaction
- (c) The above reaction is not shown by alkenes
- (d) All of these
- Which of the following compounds (i through v) should not be classified as an acetal? 148.



(a) ii and iii

(b) iv

(c) i

- (d) none (they are all acetals)
- 149. In which of reactions final product is NOT a ketone :

(a) 
$$CH_3 - C \equiv C - H \xrightarrow{NaNH_2} (A) \xrightarrow{CH_3-I} (B) \xrightarrow{HgSO_4} (C)$$

(b) 
$$H - C \equiv C - H \xrightarrow{\text{NaNH}_2} (C) \xrightarrow{\text{CH}_3 - \text{CH}_2 - \text{I}} (D) \xrightarrow{\text{Hg(OAc)}_2, \text{H}_2O} (E)$$

(c) 
$$R - C - OH \xrightarrow{\text{NaOH}} (A) \xrightarrow{\text{CH}_3-I} (B)$$

(1) BH<sub>3</sub> THF

(d) 1-butyne 
$$\xrightarrow{\text{NaNH}_2}$$
  $(A)$   $\xrightarrow{\text{CH}_3-\text{I}}$   $(B)$   $\xrightarrow{\text{(2) H}_2\text{O}_2/\text{HO}^{\Theta}}$   $(C)$ 

- The reaction of ethyl methyl ketone with Cl<sub>2</sub>/excess OH<sup>-</sup> gives the following major product 150.
  - (a) ClCH2CH2COCH3

(b) CH<sub>3</sub>CH<sub>2</sub>COCCl<sub>3</sub>

(c) ClCH<sub>2</sub>CH<sub>2</sub>COCH<sub>2</sub>Cl

- (d) CH<sub>3</sub>CCl<sub>2</sub>COCH<sub>2</sub>Cl

The product obtained from the following sequence of reactions is 
$$CH_{3} - C \equiv CH \xrightarrow{HgSO_{4}} A \xrightarrow{NaBH_{4}} B$$

- (a) propanol
- (b) 2-propanol
- (c) 1-propanol
- (d) propanhe

						ANSW	ERS	— LE	VEL 1		M e				
1.	(a)	2.	(b)	3.	(d)	4.	(c)	5.	(a)	6.	(c)	7.	(b)	8.	(b)
9.	(b)	10.	(c)	11.	(c)	12.	(c)	13.	(b)	14.	(b)	15.	(b)	16.	(b)
17.	(b)	18.	(b)	19.	(b)	20.	(d)	21.	(b)	22.	(b)	23.	(b)	24.	(d)
25.	(c)	26.	(b)	27.	(b)	28.	(a)	29.	(b)	30.	(c)	31.	(d)	32.	(c)
33.	(b)	34.	(b)	35.	(a)	36.	(b)	37.	(c)	38.	(d)	39.	(b)	40.	(a)
41.	(b)	42.	(a)	43.	(a)	44.	(b)	45.	(b)	46.	(a)	47.	(b)	48.	(d)
49.	(c)	50.	.(b)	51.	(d)	52.	(b)	53.	(b)	54.	(c)	55.	(b)	56.	(b)
57.	(a)	58.	(d)	59.	(c)	60.	(c)	61.	(c)	62.	(a)	63.	(b)	64.	(b)
65.	(b)	66.	(d)	67.	(b)	68.	(d)	69.	(b)	70.	(c)	71.	(b)	72.	(d)
73.	(d)	74.	(a)	75.	(d)	76.	(a)	77.	(a)	78.	(a)	79.	(c)	80.	(c)
81.	(d)	82.	(b)	83.	(b)	84.	(b)	85.	(b)	86.	(a)	87.	(b)	88.	(c)
89.	(b)	90.	(b)	91.	(c)	92.	(b)	93.	·(b)	94.	(b)	95.	(c)	96.	(c)
97.	(d)	98.	(b)	99.	(c)	100.	(c)	101.	(c)	102.	(c)	103.	(c)	104.	(c)
105.	(c)	106.	(b)	107.	(a)	108.	(c)	109.	· (c)	110.	(b)	111.	(c)	112.	(b)
113.	(b)	114.	(c)	115.	(c)	116.	(a)	117.	(a)	118.	(a)	119.	(b)	120.	(c)
121.	(b)	122.	(b)	123.	A-c	123.	B-b	124.	(b)	125.	(a)	126.	(c)	127.	(a)
128.	(b)	129.	(c)	130.	(a)	131.	(a)	132.	(c)	133.	(d)	134.	(a)	135.	(a)
136.	(a)	137.	(a)	138.	(b)	139.	(d)	140.	(b)	141.	(d)	142.	(a)	143.	(c)
144.	(b)	145.	(d)	146.	(b)	147.	(d)	148.	(d)	149.	(c)	150.	(b)	151.	(b)

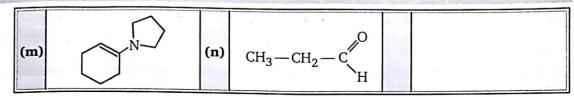


## LEVEL-2

**1.** Select the best choice for example (A to L) from the examples (a to n) given below. Write your choice in the box given.

A.	An acetal derivative of a ketone.	
B.	A chiral ketone.	
C.	An aldehyde that gives a aldol condensation with itself.	
D.	An oxime derivative	
E.	A reagent that reduces aldehydes to 1°- alcohols.	
F.	An α, β-unsaturated ketone.	
G.	A reagent that oxidizes aldehydes to carboxylic acids.	
H.	A reagent that reduces ketones to alkanes.	
I.	An enamine derivative of a ketone.	
J.	An intermediate in imine formation.	-
K.	A cyclic hemiacetal.	
L.	A cyanohydrin derivative.	

(a)	CH <sub>3</sub>	(b)	OH	(c)	
(d)	OH R——NHR' H	(e)	OH CH3	<b>(f)</b>	Zn(Hg)H <sub>3</sub> O <sup>(+)</sup>
(g)		(h)	NaBH <sub>4</sub> aq. alcohol	(i)	H
(J)	Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>(+)</sup> OH <sup>(-)</sup>	(k)	HO N	(1)	OCH <sub>3</sub>   CH <sub>3</sub> -C-OCH <sub>3</sub>   CH <sub>3</sub>



2. T	The following questions refer to the compounds (A to G) shown below:											
i.	Which of reduced borohyda	by	nds are sodium		Which c hydrolyze aqueous	ed	unds are by hot	iii.	oxidis	n com sized /pyridir		are by
A		E		A		E			A		E	
В		F		В		F		1	В		F	
C		G		C		G			C		G	
D		H		D		Н		1	0	1	H	
A.		J <sup>o</sup>	В.	C	РН	C.		) \ \ '	D.	Y	l <sub>o</sub>	<u> </u>
E.	но	)°	F.	``	O H	G.		0	н.			8

### Match the column:

	Column (I)	Column (II)				
(a)	O LiAlH₄→	(p)	racemic mixture			
(b)	O (1) KCN (2) H <sup>⊕</sup>	(q)	Diastereomers			
(c)	$Ph-CH_2-Cl \xrightarrow{KCN}$	(r)	Nu-addition reaction			
(d)	$ \begin{array}{c} O \\ \hline                                  $	(s)	Nu-Substitutions reaction			

## 4. Complete the following table.

	REACTANT	MAJOR ORGANIC PRODUCTS	
a.	CH <sub>3</sub>	H <sub>2</sub> /Pd - C in ethanol (solvent)	<b>A</b>
<b>b.</b>	$COOCH_3$	H <sup>+</sup> /H <sub>2</sub> O/Δ	В
c.	H	$(CH_3)_2 \bar{C} - P(C_6H_5)_3$	C
d.		1. Li <sup>+</sup> [(CH <sub>3</sub> ) <sub>2</sub> Cu] <sup>-</sup> in dry ether 2. H <sup>+</sup> /H <sub>2</sub> O	<b>D</b>
e.	E	OH <sup>-</sup> /ethanol/Δ	CH <sub>3</sub> O

### 5. Comprehension

Consider the following reactions and answer A and B.

- **A.** Suggest a reagent appropriate step (a) the synthesis.
  - (a)  $HO^-/Br_2$  (1 mole)

(b)  $H^{+}/Br_{2}$  (1 mole)

(c) both (a) and (b)

(d) None of these

### ALDEHYDES AND KETONES

431

**B.** Yield of each step as actually carried out in laboratory is given above each arrow. What is overall yield of the reaction?

(a) 60%

(b) 21%

(c) 40%

(d) 68%

6.

Reaction 1.	$ \begin{array}{c} O \\ C - H \\ \hline                                  $
Reaction 2.	$Ph - CH = CH - C - CH_3 \xrightarrow{Al(OCHMe_2)_3 \atop CH_3 - CH - OH} (B)$ $CH_3$
Reaction 3.	$Ph - CH = CH - CH - CH_3 \xrightarrow{(1) \text{ NaOI}} (C)$

### Degree of unsaturation present in compound (A + B + C) is?

**7.** Within each set, which compound should be more reactive toward carbonyl addition reaction?

	Α .	В
Set (1)	$CH_3 - C - CH_2 - Br$	$\begin{array}{c} O \\ \parallel \\ CH_3 - C - CH_2 - CH_2 - Br \end{array}$
Set (2)	$CH_3 - C - C - CH_3$	$\begin{array}{c} O \\ \parallel \\ CH_3 - C - CH_2 - CH_3 \end{array}$
Set (3)	$CH^3O$ — $CH = O$	$O_2N \longrightarrow CH = O$
Set (4)	С—Н	O     CH <sub>3</sub> — C — H
Set (5)	) >=0	0

Set (6)	CHO H	CHO
Set (7)	о о С—H	о с—н о с—н
Set (8)	CHO	CHO
Set (9)	C— $C$ H <sub>3</sub>	
Set (10)	$CH_3 - C - CH_2 - CH_3$	С—Н

8. Match the Column (I) and Column (II). (Matrix)

	Column (I)	Column (II)		
(A)	$ \frac{\text{HCN}}{\text{traces of KOH}} \to (A) \xrightarrow{\text{LiAlH}_4} \to (B) \xrightarrow{\text{NaNO}_2} \to (C) $	(p)	Formation of six member ring takes place	
(B)	$ \begin{array}{c}  & \xrightarrow{\text{NH}_2\text{OH}} \rightarrow (A) \xrightarrow{\text{H}^+} \rightarrow (B) \xrightarrow{\text{LAH}} \rightarrow (C) \end{array} $	(q)	Final product is Ketone	

(C)	$CH_3 - C - CH_2 - CH_2 - CH_2 - C - H \xrightarrow{HO^-} \Delta (A)$	(r)	Final product formed will give positive Tollens test
(D)	$ \begin{array}{c}  & Ph \\  & CH_3 \xrightarrow{H^{\oplus}} (A) \end{array} $	(s)	Final product formed will react with 2,4-DNP. (2,4-di-nitrophenyl hydrazine)

9. Consider reactions A through F. Those carbon atoms undergoing change, as part of a functional group, are marked as C<sup>12</sup>, C<sup>14</sup> or starred. In the cases shown, each carbon atom has either been reduced or oxidized. Your job is to identify the change in oxidation state that has occurred for each of the marked carbon.

	Reaction	C12	C14
A.	$CH_3CH = CH_2 \xrightarrow{Br_2} CH_3CHBrCH_2Br$	Reduced	Reduced
Α.	12 14	Oxidized	Oxidized
D	(i) B <sub>2</sub> H <sub>6</sub> CH CH CH CH	Reduced	Reduced
В.	$CH_{3}CH = CH_{2} \xrightarrow{(i) B_{2}H_{6}} CH_{3}CH_{2}CH_{2}OH$	Oxidized	Oxidized
_		Reduced	
C.	$CH_3CH_2$ ČH = $O \xrightarrow{NaBH_4} CH_3CH_2CH_2OH$	Oxidized	
	* Ag(+)	Reduced	
D.	$CH_3CH_2\overset{\bullet}{C}H = O \xrightarrow{Ag^{(+)}} CH_3CH_2CO_2H$	Oxidized	
	CH <sub>3</sub> COCH <sub>3</sub>	Reduced	Reduced
E.	$CH_3COCH_2 CO_2H \xrightarrow{Heat} CH_3COCH_3$ $O = C = 0$	Oxidized	Oxidized
-	$H_2 C = C(OH)C_2H_5 \xrightarrow{\text{tautomerization}} H_3CCOC_2H_5$	Reduced	Reduced
F.	$n_2 C = C(OI)C_2 n_5$	Oxidized	Oxidized

10. Consider the possible formation of an aldehyde or ketone product when each of the ten compounds in the column on the left is treated with each of the reagents shown in the top row. Check the designated answer box if you believe an aldehyde or ketone will be formed.

Assume that the reagents may be present in excess. For each checked reaction, try to draw the structure of the major product (s).

Starting	PCC C <sub>5</sub> H <sub>5</sub> NHCrO <sub>3</sub> Cl	Jone's Reagent CrO <sub>3</sub> in aq. acid	Pb(OAc) <sub>4</sub> [or HIO <sub>4</sub> ]	(i) O <sub>3</sub> , (ii) Zn dust	H₃O <sup>⊕</sup>	(i) BH <sub>3</sub> in THF (ii) H <sub>2</sub> O <sub>2</sub> + NaOH
ОН		,				
$CH_3$ $C = C - CH_3$			ar .	(8)		
CH <sub>2</sub> -OH			5 . -0.	2" 2 - 2	·	
				7	3	-
CH <sub>3</sub> OH			3	ar ar		e (8)
$CH_3$ $CH_3$ $CH_3$		a *		2 = 0 0	. 4	
$H_3C$ $C = C$ $CH_3$ $CH_3$						
CH <sub>3</sub>	*	E	8			- x-
НО						
$CH_3$ $CH_3$ $CH_3$ $C_2H_5$ $OH$					9	

### 11. Comprehension

Wittig reaction:

The reaction of a phosphorus ylide with an aldehyde (or) ketnoe introduces a carbon-carbon double bond is place of the carbonyl bond.

$$\begin{array}{c|c}
O & CH_2 \\
\parallel & \parallel \\
R - C - R + Ph_3P = CH_2 \longrightarrow R - C - R + Ph_3P = O
\end{array}$$

**Mechanism:** 

$$R - C - R + CH_2 - PPh_3$$

$$(Nucleophilic addition reaction)$$

$$O = PPh_3 + R - C - R$$

$$(Nucleophilic addition reaction)$$

$$CH_2$$

$$R - C - CH_2$$

$$(betaine intermediate)$$

$$R - C - CH_2$$

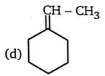
Driving force of the reaction is high bond energy of (P = O).  $(\Delta H = -ve)$ 

**A.**  $+ Ph_3P = CH_2 \longrightarrow (A)$  (major), Major product (A) is:









**B.**  $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - PPh_3 \xrightarrow{Ph-Li} (A)$ , Major product (A) is:









C.  $CH_3$   $CH_3$   $Ph_3P$  (A), Major product (A) is:

- (a) cis-2-butene
- (b) trans-2-butene
- (c) iso-butene
- (d) 1-butene

**D.** 
$$CH_3 - C - (CH_2)_3 - C - CH_2 - P(OEt)_2 \xrightarrow{NaH} (A)$$
 (cyclic). Product (A) is:

**E.** Identify major product in given intramolecular Wittig reaction :

Rxn.-1 
$$\longrightarrow$$
 CH<sub>3</sub>  $-$  C $-$  CH<sub>2</sub>  $-$  CH(CO<sub>2</sub>Et)<sub>2</sub>  $+$  H<sub>2</sub>C  $=$  CH  $\oplus$  PPh<sub>3</sub>  $\xrightarrow{\text{NaH}}$  (A)

Rxn.-2 
$$\longrightarrow$$
  $CH = O$   
 $ONa$   $+ H_2C = CH - {}^{\oplus}PPh_3 \longrightarrow (B)$ 

Product (A) and (B) respectively are:



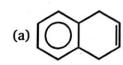


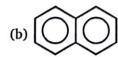


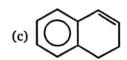
F. 
$$CH_2 - Br$$

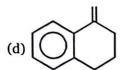
$$CH_2 - Br \xrightarrow{\text{(1) Ph}_3P(2 \text{ mole})} (A) \text{ ; product (A) is :}$$

$$CH_2 - Br \xrightarrow{\text{(2) 2Ph}-Li} (A) \text{ ; product (A) is :}$$









### 12. Match the column:

	Column (I)		Column (II)		
	Conversion	Reagent			
(a)	$\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & & $	(p)	$\mathrm{NH_2/NH_2/HO^{\Theta}}$ , $\Delta$ (Wolff-Kishner reduction)		
(b)		( <b>q</b> )	Zn(Hg), HCl (Clemmensen reduction)		
(c)	$0 \longrightarrow 0 \longrightarrow 0$ $0 \longrightarrow 0$	(r)	LiAlH <sub>4</sub>		
(d)	$\stackrel{\text{OH}}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow} \stackrel{\text{OH}}{\longrightarrow}$	(s)	None		

### 13. Comprehension

$$(A) \xrightarrow{\text{HgSO}_4} (B) \xrightarrow{\text{(1) NaBH}_4} \text{CH}_3 \xrightarrow{\text{--C--CH}_2 \text{---CH}_3}$$
$$|| \text{CH---CH}_3$$

### **A.** Reactant (A) is:

(a) 
$$CH_3$$
— $C \equiv C$ — $CH$ — $CH_3$ 

$$CH_3$$

(c) 
$$CH_3$$
— $CH$ — $C \equiv CH$   
 $CH_2$ — $CH_3$ 

(b) 
$$HC \equiv C - C - C - C$$

(d) 
$${\rm CH_3}{-\!\!\!\!\!-}{\rm C} \equiv {\rm C}{-\!\!\!\!\!-}{\rm CH_2}{-\!\!\!\!\!-}{\rm CH_2}{-\!\!\!\!\!-}{\rm CH_3}$$

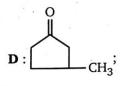
### **B.** Product (*B*) is:

### ANSWERS — LEVEL 2

1. 
$$A-l$$
;  $B-g$ ;  $C-n$ ;  $D-k$ ;  $E-h$ ;  $F-c$ ;  $G-j$ ;  $H-f$ ;  $I-m$ ;  $J-d$ ;  $K-e$ ;  $L-b$ 

2. 
$$i - A, B, C, E, F$$
;  $ii - D, G, H$ ;  $iii - B, E, F$ 

 $\mathbf{A}: \operatorname{Ph} - \operatorname{CH}_{-} \operatorname{CH}_{3}; \quad \mathbf{B}: \operatorname{Ph} - \operatorname{CH}_{2} - \operatorname{COOH};$ 



5. 
$$A - b$$
;  $B - b$ 

**6.** 
$$A + B + C = 17$$

7. set 1 - A; set 2 - A; set 3 - B; set 4 - B; set 5 - A; set 6 - B; set 7 - B; set 8 – B; set 9 – A; set 10 – B

8. 
$$A - p, q, s; B - p; C - p, q, s; D - p, q, s$$

**9.** A: both are oxidized;  $B:C^{12}$  is reduced,  $C^{14}$  is oxidized; C: reduced; D: oxidized  $E:C^{12}$  is reduced,  $C^{14}$  is oxidized;  $F:C^{12}$  is reduced,  $C^{14}$  is oxidized

10.

10.						
Compound	PCC C <sub>5</sub> H <sub>5</sub> NHCrO <sub>3</sub> Cl	Jone's Reagent CrO <sub>3</sub> in aq. acid	Pb(OAc) <sub>4</sub> [or HIO <sub>4</sub> ]	(i) O <sub>3</sub> , (ii) Zn dust	<sup>+</sup> О <sub>8</sub> Н	(i) BH <sub>3</sub> in THF (ii) H <sub>2</sub> O <sub>2</sub> + NaOH
OH			×	×	×	X.
$CH_3$ $C = C - CH_3$	×	×	, <b>X</b>		>	<b>V</b>
СН2-ОН	1	1	×	<b>✓</b>	X	×
	×	×	<b>X</b>	1	×	×
CH <sub>3</sub> OH		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	<b>X</b> .	<b>/</b>	· / ,	1
$CH_3$ $CH_3$ $CH_3$	×	X	×	×	×	×
$H_3C$ $C = C$ $CH_3$ $CH_3$	X	4 <b>X</b>	×	1	ý	<b>√</b>
CH <sub>3</sub>	×	X	×	1	1	
НОООН	1	<b>√</b>	X	X	X	Х
$CH_3$ $CH_3$ $CH_5$ $CH_5$ $CH_5$	√ ✓	<b>/</b>	1	×	X	×

**<sup>11.</sup>** A-a; B-a; C-b; D-b; E-a; F-b

**<sup>13.</sup> A.** (c) **B.** (d)

## **ALDOL AND CANNIZARO REACTION**



# LEVEL- 21

**1.** Compound *A* and *B*, both were treated with NaOH, producing a single compound *C*.

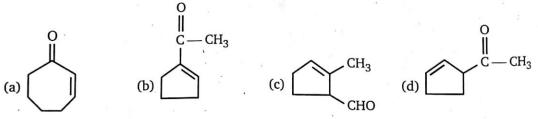
2. 
$$CH_3$$
 ?  $CH_3$  ; This conversion can be achieved by :

- (a) Dehydration, Hydrolysis
- (b) Retro aldol and further condensation
- (c) Perkin condensation & Clemmensen reduction
- (d) Clemmensen and Perkin condensation
- 3. This is an example of an intramolecular aldol reaction :

(a) 
$$H_2SO_4 \rightarrow (A)$$
; Product  $(A)$  is :

(b)  $C$ 
(c)  $C$ 
(d)

4. 
$$CH_3 - C - CH_2 -$$



- **5.** Ph CH = CHCHO + CH<sub>3</sub>CH = CHCHO  $\xrightarrow{\text{base}}$  (A) 87%; Product of this reaction is:
  - (a)  $Ph (CH = CH)_2 CHO$
- (b)  $Ph (CH = CH)_3CHO$
- (c)  $Ph (CH = CH)_4CHO$
- (d)  $Ph CH = CH CH = CH CH_3$
- **6.** CH<sub>3</sub>CHO  $\xrightarrow{10\% \text{ NaOH}} \xrightarrow{\Delta} \xrightarrow{\text{H}_2} (A)$ ; Product (A) of the reaction is:
  - (a) propanol
- (b) ethanol
- (c) butanol
- (d) pentanol

7. (A) 
$$\xrightarrow{\text{NaOH}} \Delta$$

Reactant (A) is:

(d) 
$$CH_3 - C - (CH_2)_4 - CH_2 - OH$$

8. 
$$CH_3 - C - CH_2 - C - CHO \xrightarrow{KOH, H_2O} (A)$$
; Product A is:

9. 
$$\underbrace{\frac{\text{LDA}}{\text{CH}_3-\text{CH}_2-\text{I}}}_{\text{CH}_3-\text{CH}_2-\text{I}} (A); \text{ Product } A \text{ is:}$$

$$CHO$$
 + conc. NaOH  $\xrightarrow{heat}$ , products Identify the product.

**11.** Compare enolate A with enolate B.

Which of the following statements is true?

- (a) A is more stable than B
- (c) B is more stable than A
- (b) A and B have the same stability
- (d) No comparison of stability can be made

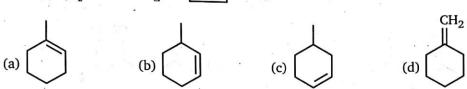
12. Benzalacetone is the product of mixed aldol condensation between benzaldehyde  $(C_6H_5CH=O)$  and acetone  $[(CH_3)_2C=O]$ . What is its structure?

(a) 
$$C_6H_5CH = CHCCH_3$$
 (b)  $C_6H_5CH = C(CH_3)_2$  (c)  $C_6H_5CCH = CHCCH_3$  (d)  $C_6H_5CCH = CH_2$ 

**13.** Identify the major product *P* in the following reaction:

Product (B) is:

15. 
$$(A) \xrightarrow{(i) O_3} (B) \xrightarrow{NaOH} C - CH_3$$
 the reactant (A) will be:



**16.** Identify the principal product of the following reaction?

17. Which one of the following compounds is the best choice for being prepared by an efficient mixed aldol addition reaction?

**18.** Identify the major product *P* in the following reaction:

OLi OLi
$$(i) CH_3CH_2I/THF \rightarrow F$$
OEt

20.

**19.** The enolate ion that reacts with 3-buten-2-one to form (*Y*) is :

(a) 
$$\ominus$$
(b)  $\ominus$ 
(c)  $\ominus$ 
(d)  $\ominus$ 
(d)  $\ominus$ 
(d)  $\ominus$ 
(d)  $\ominus$ 
(e)  $\ominus$ 
(f)  $\ominus$ 
(f)  $\ominus$ 
(f)  $\ominus$ 
(g)  $\ominus$ 
(h)  $\ominus$ 
(h)

Product (B) in the above reaction is:

**21.** H  $\stackrel{\text{II}}{-}$  D  $\stackrel{\text{HO}^-}{-}$ ; Product of this Cannizaro reaction is :

(a) 
$$D - CO_2^- + CH_2DOD$$

(b) 
$$H - CO_2^- + D - CO_2^-$$

(c) 
$$D - CO_2^- + CH_2DOH$$

(d) 
$$D - CO_2^- + CHD_2OH$$

An organic compound with the molecular formula C9H10O forms a 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizaro reaction, on vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Structure of organic compound is:



23. 
$$CH_3$$
— $C$ — $CH_2$ — $C$ — $C$ 

Number of intramolecular aldol condensation product is:

- (b) 2
- (d) 4

**24.** 
$$(A) \xrightarrow{C_7 H_{14}} \xrightarrow{C_1/AcOH} (B) + (C)$$

Compound (A) exist in geometrical isomers and (B) gives Cannizaro reaction.

(*A*) will be :

(b) 
$$(CH_3)_3CCH_2 - CH = CH_2$$

(c) 
$$(CH_3)_3C - CH = CH - CH_3$$

$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3 - CH_2 - CH = CH_2$   $CH_3 - CH_2 - CH = CH_2$ 

- Which of the following compounds will not undergo Cannizaro reaction, when treated with 25. 50% aqueous alkali?
- (c) Me<sub>2</sub>CHCHO
- (d)  $Ph CH_2 CHO$

26. 
$$H = C - D \xrightarrow{H^{18}O^{-}} D = C - 18O^{-} + CH_{2}D = OH$$

Above reaction is known as:

- (a) Cannizaro reaction, Disproportionation reaction
- (b) Tischenko reaction, Disproportionation reaction
- (c) Cross Cannizaro reaction, Redox reaction

, Aldol condensation

, Perkin reaction

, Cannizaro reaction

$$\mathrm{CH} = \mathrm{CH} - \mathrm{CO_2H}$$
 , Claisen-condensation

29. Choose the most reasonable reaction intermediate for the following reaction.

30. 
$$CH_3 - CH - CH_2 - C - H \xrightarrow{HO^-} (A)$$
; 3HCHO +  $A \xrightarrow{Na_2CO_3} (B)$  (82%)

Product (B) of the above reaction is:

$$\begin{array}{c} \text{CH}_2-\text{OH} & \text{CHO} \\ | \\ \text{(a) HO}-\text{CH}_2-\text{C}-\text{CH}_2\text{OH} & \text{(b) HO}-\text{CH}_2-\text{C}-\text{CHO} \\ | \\ \text{CH}_2-\text{OH} & \text{CH}_2-\text{OH} \end{array}$$

$$\begin{array}{c} \text{CH}_2\text{OH} & \text{CHO} \\ | & | \\ \text{(c)} \text{ HO} - \text{CH}_2 - \text{C} - \text{CH}_2\text{OH} \\ | & | \\ \text{CHO} & \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ | & | \\ \text{CH}_2 - \text{OH} & \text{CH}_2 - \text{OH} \\ \end{array}$$

**31.** CH<sub>3</sub>CH = CHCHO 
$$\xrightarrow{\text{OH}^-} \xrightarrow{\Delta} A$$
; Product A is:

- (a)  $CH_3(CH = CH)_3CHO$
- (b)  $CH_3CH_2CH_2(CH = CH)_2CHO$
- (c)  $CH_3(CH_2CH_2)_3CH = CH CHO$
- (d) none is correct

32. 
$$\underbrace{\frac{HO^{\bigcirc}}{H_2O}}_{(A)} B.$$
 (A) and (B) are isomer: Identify (B).

(c) 
$$C - CH_3$$

34. 
$$+ \longrightarrow H$$
  $\xrightarrow{HCl/heat} A$ . Product (A) is

(b) 
$$Ph - C - CH_2 - CH_2 - Ph$$

(c) 
$$Ph - CH = CH - CH - Ph(d)$$
  
OH

(d) 
$$Ph - CH = C = CH - Ph$$

**35.** Which of the following reactant on reaction with conc. NaOH followed by acidification gives the following lactone as the product ?

(a) 
$$C-OCH_3$$
  $CO_2H$ 

37. 
$$(P) \xrightarrow{KOH} \stackrel{O}{\xrightarrow{\Delta}} Ph-CH_2-OH + Ph-CO_2^{\circ}$$

(R)  $\xrightarrow{O_3} P + Q$ , Structure of (R) is:

(a) 
$$Ph - CH = CH - CH_3$$

(b) Ph—CH=
$$C < CH_3$$

$$CH_3$$
(c) Ph—C=CH—CH<sub>3</sub>

38. The following reaction gives:

(a) 
$$OMe$$
 +  $CH_3OH$  OMe

(b) 
$$OMe$$
 +  $HCO_2^{\circ}$ 

(d) 
$$OMe$$
 +  $CH_3OH$ 

Which of the following is not the product of an intramolecular aldol condensation? 39.

**40.**  $x = \text{no. of compound better hydride donor than Ph-$ H

(d) 
$$CH_3$$
  $CH_3$   $O^{\ominus}$ 

**41.** Choose the reactant whose aldol reaction would give jasmone.

**42.** Compound *X* undergoes the following reaction sequence. What is the structure of compound *X*?

$$X \xrightarrow{\text{NaOH}} \xrightarrow{\text{Heat}} \xrightarrow{\text{H}_2/\text{Pd}} \xrightarrow{\text{1.LiAlH}_4} \xrightarrow{\text{2H}_2\text{O}}$$

$$(a) \text{ (b) HO}$$

$$(c) \text{ (d) O}$$

43. Predict the major product of the following reaction sequence

$$(a) \qquad \begin{array}{c} CH_3 + \text{NaOH} & \xrightarrow{H_3C} & \xrightarrow{H_2O} & \xrightarrow{1.} & \xrightarrow{2. H_2O} \\ \\ (b) & & & \\ CH_3 & & & \\ (b) & & & \\ CH_3 & & \\ CH_3 & & \\ CH_3 & & & \\ CH_5 & &$$

$$(c) \qquad (d) \qquad (d) \qquad CH_3$$

44. CHO 
$$\xrightarrow{\text{Conc. KOH}}$$
  $(A) \xrightarrow{\text{H}^{\oplus}}$   $(B)$  Cyclic product

Structure of (B) is:

						ANSW	ERS	— LE	VEL 1						
1.	(a)	2.	(b)	3.	(a)	4.	(b)	5.	(b)	6.	(c)	7.	(b)	8.	(b)
9.	(b)	10.	(c)	11.	(a)	12.	(a)	13.	(a)	14.	(b)	15.	(a)	16.	(b)
17.	(b)	18.	(a)	19.	(c)	20.	(a)	21.	(c)	22.	(b)	23.	(c)	24.	(c)
25.	(d)	26.	(a)	27.	(c)	28.	(b)	29.	(c)	30.	(c)	31.	(a)	32.	(a)
33.	(c)	34.	(a)	35.	(c)	36.	(b)	37.	(b)	38.	(b)	39.	(c)	40.	(b,c)
41.	(d)	42.	(d)	43.	(c)	44.	(a)						(-)		(2,0)



# LEVEL-2

### 1. Comprehension

Mechanism of Cannizzaros reaction of benzaldehyde is

**A.** Which of the following reactants can undergo Cannizaro's reaction.?

(b) R<sub>3</sub>CCHO

(d) All of these

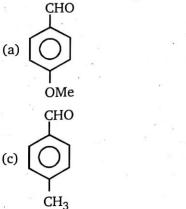
- B. Order of the above reaction is:
  - (a) 1

(b) 2

(c) 3

(d) 4

C. Which of the following is best hydride donor in Cannizaro's reaction?



(b) NO<sub>2</sub> CHO

(d) CI

- D. Cannizaro's reaction is:
  - (a) Reduction

(b) Disproportionation reaction

(c) Oxidation

- (d) Ion exchange reaction
- E. Which of the following cannot undergo intramolecular Cannizaro's reaction?

2. Aldol condensation proceeds by carbon-carbon bond formation between an enolate donor and a carbonyl acceptor. For each of the following aldol products (a through e) select a donor and an acceptor compound from the list at the bottom of the page (compounds A through H). Write the letter corresponding to your selection in the appropriate answer box.

9	Aldol Product	Donor	Acceptor
a.	OH		
ъ.	ОН		
c.	CH—		
d.	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> COCH <sub>3</sub>		
e.	$\begin{array}{c} CO_2C_2H_5 \\ \\ CO_2C_2H_5 \end{array}$		

### 3. Comprehension

During an experimental workup procedure, a chemist treated a starting material with NaOH in the solvent acetone  $[(CH_3)_2C=O]$ ; however, the starting material was recovered unreacted. Instead, the chemist isolated a small amount of Product A (shown below).

#### **Product A**

The chemist determined that Product A resulted from the aldol self-condensation of acetone. Product A was identified based on the following observations.

Observations about Product A

- Elemental analysis of Product A indicated that it consisted only of carbon, hydrogen, and oxygen.
- 2. product A had a molecular weight of 116 g/mol.
- 3. Product A was a methyl ketone because it gave a positive iodoform test.
- 4. When product A was treated with Br<sub>2</sub> in CCl<sub>4</sub>, the red bromine colour persisted, because no carbon-carbon double bonds were present to react with the bromine.

The structure of Product A was further confirmed when treatment with hot sulfuric acid resulted in the corresponding dehydration product, Product B.

- A. What is the molecular weight of a compound that undergoes an aldol self-condensation reaction to result in a  $\beta$ -hydroxy ketone with a molecular weight of 144?
  - (a) 70 g/mol

(b) 72 g/mol

(c) 74 g/mol

- (d) 76 g/mol
- **B.** The aldol self-condensation of acetone is an equilibrium that favours acetone over its condensation product. Which of the following experimental modifications is most likely to shift the position of equilibrium toward Product A?
  - (a) Using only a catalytic amount of NaOH
  - (b) Using only a catalytic amount of acetone
  - (c) Removing Product A as it is formed
  - (d) Increasing the reaction temperature to the boiling point of acetone
- C. Based only on observation 1 and 2, which of the following compounds could have been Product A?

(c) 
$$CH_2 = CHCH_2 - O - CH_2CH_2CH_3$$

- **D.** When a drop of Br<sub>2</sub> in CCl<sub>4</sub> is added to Product B, the resulting solution will be:
  - (a) colourless, because Product B does not contain a carbon-carbon double bond
  - (b) colourless, because Product B contains a carbon-carbon double bond
  - (c) red, because Product B does not contain a carbon-carbon double bond
  - (d) red, because Product B contains a carbon-carbon double bond
- E. Which of the following compounds from the passage will give a positive iodoform test?
  - (a) Product A only

- (b) Product A and Product B
- (c) Product A and acetone only
- (d) Product A, Product B, and acetone

### 4. Comprehension

- **A.** Structure of *A* is :
  - (a)  $H_2C = CH CHO$

(c) 
$$Ph - C = CH_2$$
  
 $CH_2$ 

- (b)  $Ph CH = CH CH_3$
- (d)  $Ph CH = C CH_3$
- **B.** Structure of (B) and (C) differentiated by:
  - (a) Tollen's reagent
  - (c) 2,4-DNP

- (b) Fehling solution
- (d) NaHSO<sub>3</sub>

**C.** Structure of *E* is :

### SUBJECTIVE PROBLEMS

X = Number of compound obtained by aldol reaction

Y =Number of compounds react with NaHCO<sub>3</sub>

Sum of X + Y is

**2.** In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is:

$$\begin{array}{c}
1 \text{ O}_{3} \\
\hline
2. \text{Zn,H}_{2}\text{O}
\end{array}$$

$$Y \xrightarrow{1. \text{NaOH} (aq)} 2 \text{ heat}$$

3. 
$$CH_3 - C - CH_3 + x HCHO \xrightarrow{KOH} HO \xrightarrow{HO} OH$$

x = moles of HCHO consumed.

Value of (x) will be

4. 
$$CH_3 - C - CH_3 + CH_3 - CH_2 - C - CH_3 \xrightarrow{KOH(aq.)} (X)$$

X = number of aldol condensation product (including stereoisomer). Find out the value of (X).

### ANSWERS — LEVEL 2

1. 
$$A-d$$
;  $B-c$ ;  $C-a$ ;  $D-b$ ;  $E-c$ 

3. 
$$A - b$$
;  $B - c$ ;  $C - d$ ;  $D - b$ ;  $E - d$ 

**4.** 
$$A - b$$
,  $B - b$ ,  $C - c$ 

### **Subjective Problems**

**1.** 6 **2.** 3 **3.** 6

6 4.9