

Worked Solutions for Organic Chemistry Revision (MCQ)**Answer Key:**

1	D		28	A		55	A		82	B		109	B		136	A		163	D
2	D		29	C		56	C		83	A		110	A		137	D		164	B
3	A		30	B		57	C		84	A		111	D		138	C		165	D
4	C		31	B		58	C		85	B		112	C		139	D		166	A
5	C		32	D		59	B		86	A		113	B		140	A		167	A
6	B		33	C		60	B		87	A		114	B		141	D		168	B
7	C		34	B		61	C		88	D		115	D		142	C		169	B
8	C		35	B		62	D		89	D		116	B		143	C		170	D
9	C		36	B		63	C		90	A		117	B		144	D			
10	C		37	C		64	D		91	C		118	C		145	A			
11	B		38	A		65	D		92	C		119	B		146	C			
12	D		39	B		66	C		93	C		120	B		147	D			
13	A		40	C		67	C		94	B		121	D		148	D			
14	C		41	C		68	C		95	D		122	A		149	D			
15	C		42	D		69	B		96	B		123	B		150	A			
16	B		43	C		70	D		97	D		124	D		151	D			
17	D		44	D		71	C		98	D		125	D		152	A			
18	C		45	C		72	A		99	C		126	A		153	A			
19	D		46	A		73	D		100	A		127	D		154	A			
20	A		47	B		74	B		101	B		128	B		155	B			
21	C		48	A		75	B		102	A		129	A		156	C			
22	C		49	A		76	A		103	D		130	D		157	B			
23	C		50	B		77	D		104	D		131	D		158	A			
24	C		51	D		78	C		105	A		132	C		159	D			
25	D		52	D		79	C		106	B		133	B		160	B			
26	B		53	A		80	D		107	A		134	C		161	B			
27	C		54	D		81	C		108	B		135	C		162	B			

General properties of organic compounds1. **D**

<u>Structure</u>	<u>Implication on Reactivity</u>
Benzene consists of delocalised π electrons above and below the plane.	Susceptible to attack by electrophiles
The ring of delocalised π electrons gives benzene additional aromatic stability .	Reaction that destroys the aromatic ring requires an additional input of energy and is thus unfavourable.

- As such, even though benzene is highly unsaturated, it does not undergo addition reactions.
- Instead, benzene mostly undergoes **substitution** reactions.

2. **D**

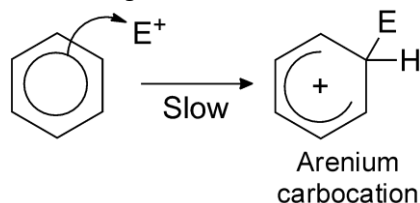
Option A: A catalyst is used to generate **strong electrophile** E^+ .

(e.g. $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$ $conc\ HNO_3 + conc\ H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$)

Option B: The carbon atom that forms a bond with the incoming E^+ becomes **sp^3 hybridised**.

Option C: There is a loss of H hence the relative molecular mass of the organic product is 34.5 greater than that of benzene.

Option D: During the rate-determining step (SLOW STEP), two of the six π electrons are used to form a dative bond with E^+ . This leaves **four π electrons delocalized** over the remaining five carbon atoms in the positively-charged arenium carbocation intermediate.

3. **A**

Both butanal and pentane are simple covalent molecules. Butanal has stronger permanent dipole- permanent dipole interactions due to the net dipole moment in (C=O) as compared to pentane which has weaker instantaneous dipole-induced dipole interactions between molecules. More energy is thus required to overcome the stronger permanent dipole-permanent dipole in butanal resulting in higher boiling point.

*Only intermolecular forces of attraction are broken during boiling of simple covalent molecules. Butanal is not able to form H-bonding with another butanal molecule due to lack of protonic H.

4. **C**

In crystalline form, amino acids exist as **zwitterions** which are held by **strong ionic bonds**. Large amount of energy is required to overcome the strong ionic bonds between the zwitterions, hence it has a higher melting point.

5.

C

To reduce pollution from motor cars, **catalytic converters containing rhodium, platinum and or palladium** are fixed onto the motor car exhaust pipes. These catalysts catalyse the **redox reactions** that convert the more harmful **C, CO, NO, NO₂** and unburnt hydrocarbons to less harmful or harmless compounds of **CO₂, H₂O, N₂ and O₂**.

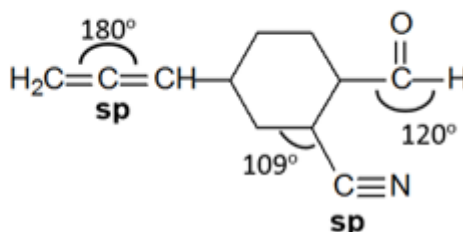
E.g. hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen



*CO cannot react directly with C_xH_y in a redox reaction to produce CO₂

6. **Answer : B (1 and 3 are correct)**

26 σ and 5 π bonds.



7. **Answer: C (3 only)**

N.B. H-bonding > pd-pd > id-id only if size of electron cloud of molecules are similar.

- the electronegativity difference between the halogen and carbon should decrease from C-Cl to C-I
Statement **does not** explain for the trend of increasing boiling point from CH₃CH₂Cl to CH₃CH₂I.
- the strength of permanent dipole-permanent dipole attraction decreases from C-Cl to C-I
The statement of option 2 is **incorrect** and **does not** explain for the trend of increasing boiling point from CH₃CH₂Cl to CH₃CH₂I.
- the strength of instantaneous dipole-induced dipole attraction increases from CH₃CH₂Cl to CH₃CH₂I
Statement is **correct** as the electron cloud size increases from CH₃CH₂Cl to CH₃CH₂I leading to the increase in id-id attraction as the dipole are more easily induced, the boiling point increases from CH₃CH₂Cl to CH₃CH₂I.
- the bond energy of C-X bond decreases from C-Cl to C-I
Statement is correct but boiling does not break the C-X bond, so this **does not** explain for the trend of increasing boiling point from CH₃CH₂Cl to CH₃CH₂I.

8. **C**

Percentage of s character of hybridised orbitals are in order $sp > sp^2 > sp^3$.

The higher the percentage of s character, the shorter the bond formed as the hybridised orbital will be nearer to nucleus and undergoes a more effective overlap.

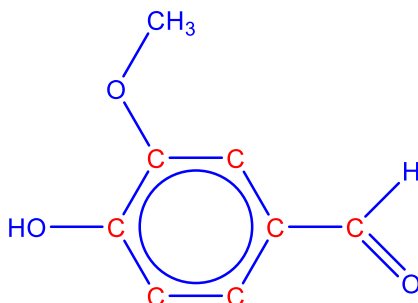
Option A has sp^3-sp^3 overlap.

Option B and D has sp^3-sp^2 .

Option C has sp^2-sp^2 overlap.

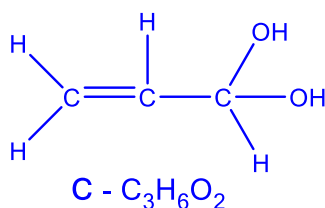
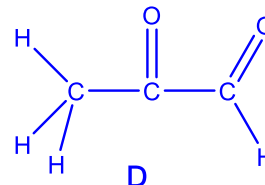
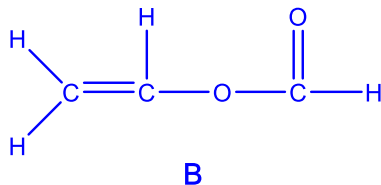
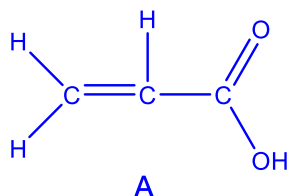
9. **C**

The 7 sp^2 hybridised carbons are shown in red, each with 3 σ bonds and 1 π bond.



10. C

As shown A, B and D are possible, but a molecule with an alkene and two alcohol groups would need 2 more H atoms, hence molecular formula $C_3H_6O_2$ (one more degree of saturation)

**Combustion of organic molecules**

11. B

In alkane, $y = 2x + 2 \therefore n(O_2) = x + \left(\frac{2x+2}{4}\right) = 1.5x + 0.5$

So the graph should be a straight line with a positive gradient which is option **B**.

Alternatively

alkane = CH_4 ; $n(O_2) = 2$

C_3H_8 ; $n(O_2) = 5$

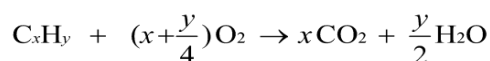
C_2H_6 ; $n(O_2) = 3.5$

C_4H_{10} ; $n(O_2) = 6.5$

As the number of carbon increases, the increase in $n(O_2)$ is increasing at a constant rate. So the relationship should be a straight line with a positive gradient which is option **B**.

12. D

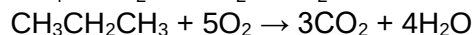
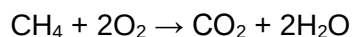
	C_xH_y	O_2	$\rightarrow$	CO_2	H_2O
Reacting vol. / cm^3	15	90		60	-
Reacting molar ratio	1	6		4	-



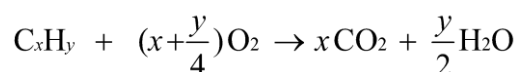
$x = 4$ hydrocarbon contains 4 C atoms

$y = 8$ hydrocarbon contains 8 H atoms

Hence, hydrocarbon is C_4H_8 .

13. **A**Avogadro's law: $V \propto n$ at constant p and T 
 $\frac{y}{2} \text{ cm}^3$ of CH_4 will produce $\frac{y}{2} \text{ cm}^3$ of CO_2
 $\frac{y}{2} \text{ cm}^3$ of $\text{CH}_3\text{CH}_2\text{CH}_3$ will produce $\frac{3y}{2} \text{ cm}^3$ of CO_2 because 1 mole of propane give 3 moles of CO_2 .

$$\text{Total } v(\text{CO}_2) = \frac{y}{2} + \frac{3y}{2} = 2y \text{ cm}^3$$

14. **C**Amount of hydrocarbon = $100 / 24000 = 0.00417 \text{ mol}$ Amount of water produced = $0.225 / 18.0 = 0.0125 \text{ mol}$ Amount of CO_2 produced = $200 / 24000 = 0.00833 \text{ mol}$ $\text{C}_x\text{H}_y : \text{CO}_2 = 1 : 2$ Hence $x = 2$ $\text{C}_x\text{H}_y : \text{H}_2\text{O} = 1 : 3$ Hence $y = 6$ 15. **C**1st reduction in the total volume of gaseous products due to cooling $\therefore$ hot $\text{H}_2\text{O}(\text{g})$ has condensed to form $\text{H}_2\text{O}(\text{l})$ at r.t.p. $\therefore$ thus, vol of $\text{H}_2\text{O}(\text{g}) = 90 - 50 = 40 \text{ cm}^3$ 2nd reduction in the total volume of gaseous products due to reaction with $\text{KOH}(\text{aq})$ $\text{CO}_2(\text{g})$ is an acidic gas and reacts with $\text{KOH}(\text{aq})$ via acid-base reaction $\therefore$ vol of $\text{CO}_2(\text{g}) = 40 \text{ cm}^3$ Thus, $\text{CO}_2(\text{g}) : \text{H}_2\text{O}(\text{g})$

$$= 40 : 40$$

$$= 1 : 1$$

Thus, $\text{C} : \text{H}$

$$= 1 : 2 \text{ (Every 1 mole of } \text{H}_2\text{O} \text{ contains 2H)}$$

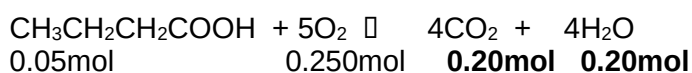
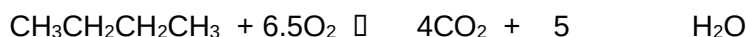
Thus the organic compound must have a ratio $\text{C} : \text{H} = 1 : 2$.

1	CH_2CH_2	$\text{C}:\text{H} = 1:2$	correct
2	$\text{CH}_3\text{CO}_2\text{H}$	$\text{C}:\text{H} = 1:2$	correct
3	$\text{CH}_3\text{CH}_2\text{CH}_3$	$\text{C}:\text{H} = 3:8$	incorrect
4	$\text{CH}_2\text{CHCH}_2\text{OH}$	$\text{C}:\text{H} = 1:2$	correct

Calculations involving Organic Molecules

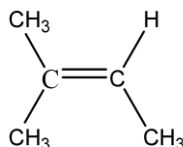
16. **B**
 0.01 mol of Compound X requires 0.03 mol of NaOH for hydrolysis. Hence 0.02 mol of NaOH is left for neutralisation with HCl.
 0.01 mol of Compound Y requires 0.01 mol of NaOH for hydrolysis of the CN group. Hence 0.04 mole of NaOH is left for neutralisation with HCl.
 0.01 mol of Compound Z requires 0.02 mol of NaOH for nucleophilic substitution reaction. Hence 0.03 mol of NaOH is left for neutralisation with HCl.

17. **D**
 Option A and D will not be further oxidised hence solution will remain orange in colour.



18. **C**

Test	Deductions
Reacts with hot acidified KMnO_4	Oxidative cleavage of $\text{C}=\text{C}$
Product reacts with 2,4-DNPH	Presence of carbonyl compound
Product does not give white ppt with limewater	No CO_2 produced $\rightarrow$ no terminal alkene



19. **D**
 $\text{CH}_2=\text{CHCH}_2\text{CN} + 3\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

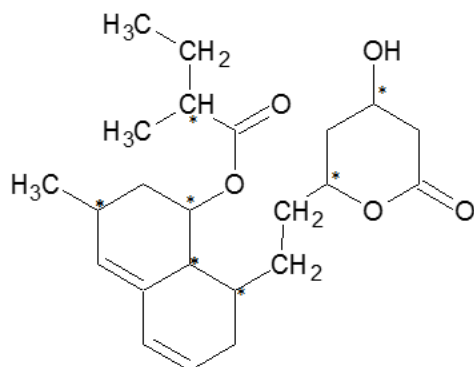
$$3 \text{ mol of } \text{H}_2 \text{ is required hence volume of } \text{H}_2 \text{ required} = 3 \times 22.7 \text{ dm}^3 \\ = 68.1 \text{ dm}^3$$

20. **A**
 1 mole of NaOH is required for hydrolysis of ester, 1 mol of NaOH is required for nucleophilic substitution of Br and 1 mol of NaOH is required for alkaline hydrolysis of CN group. Hence 0.02 mol of NaOH is left for neutralisation with H_2SO_4 .
 $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4$
 $0.02\text{mol} \quad 0.01\text{mol}$
 For 0.01 mol of H_2SO_4 , 10cm^3 is required.

Isomerism

21. **C**
 Option A: trans-trans
 Option B: cis-trans
 Option C: cis-cis
 Option D: trans-cis

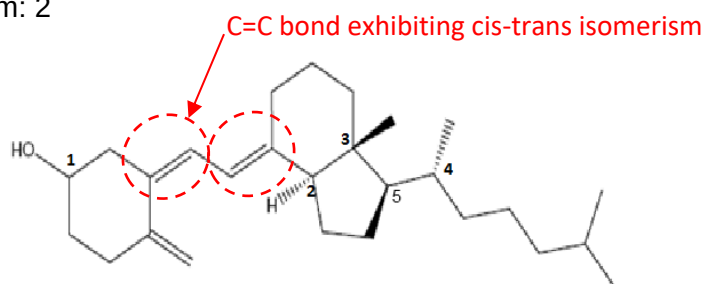
22. **C**



lovastatin

23. **C**
 In general, a molecule with **m** C=C that exhibits cis-trans isomerism and **n** chiral centers has a *maximum* of 2^{m+n} stereoisomers

m: 2



n: 5

Hence number of stereoisomers = 2^7

24. **C**
-

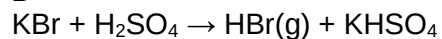
Number of stereoisomers = $2^{m+n} = 2^4$

where m = no. of C=C bond exhibiting cis-trans isomerism

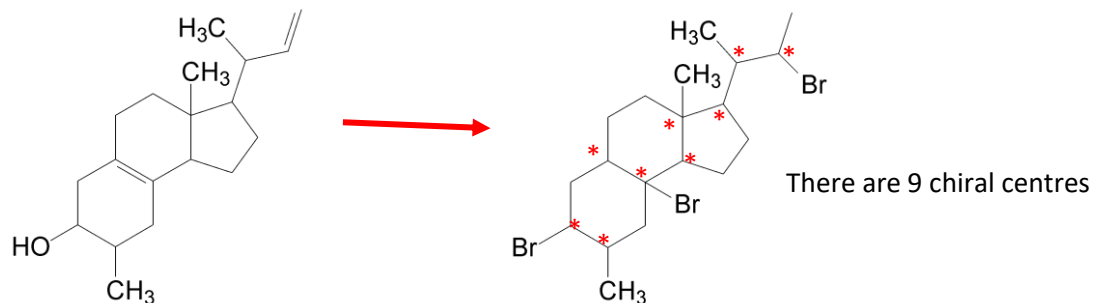
n = no. of chiral C

no chiral C in this molecule

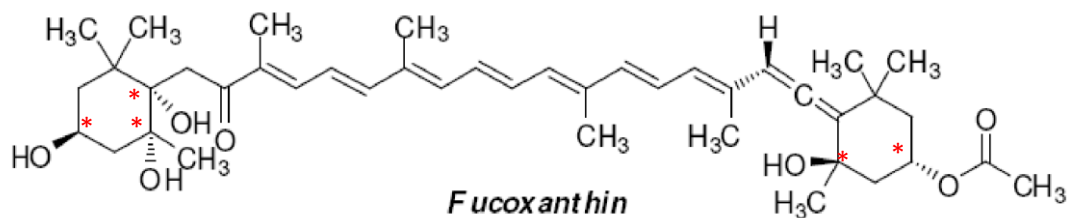
25.

D

Compound S undergoes electrophilic addition and nucleophilic substitution with HBr(g).

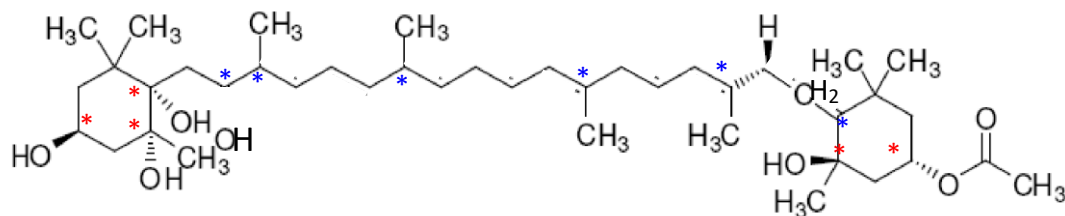


26.

B

There are 5 chiral centres in Fucoxanthin.

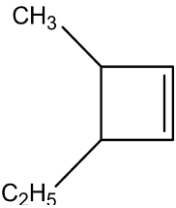
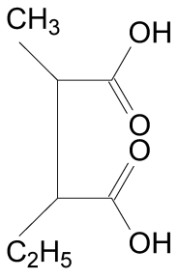
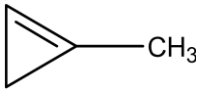
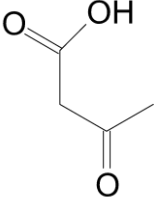
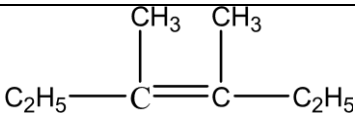
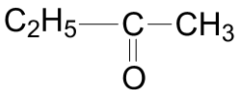
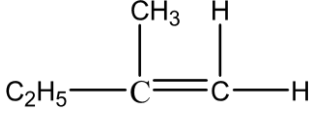
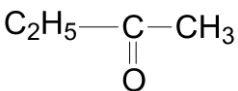
During hydrogenation, ketone is reduced to 2° alcohol and hydrogen atoms are added across C=C bonds.



There are total of 11 chiral centres and hence, 6 new chiral centres are formed.

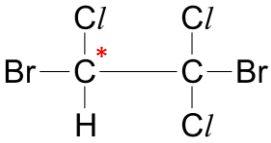
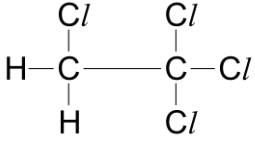
27.

C

		Organic product obtained after vigorous oxidation with hot, acidified KMnO_4
A		
B		
C	 cis-trans isomerism due to two non-identical substituents attached to each C of the C=C bond	 butanone
D	 No cis-trans isomerism due to two identical H atoms attached to C of the C=C bond	 butanone

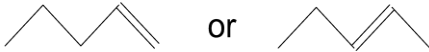
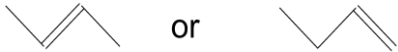
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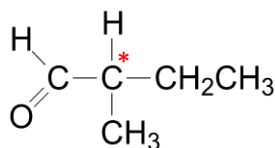
A

	Products
A	 Electrophilic addition of Br_2
B	 Electrophilic addition of HCl
C	no reaction
D	no reaction

29. **C**

During dehydration, OH is removed with H atom found on the adjacent C next to C-OH.

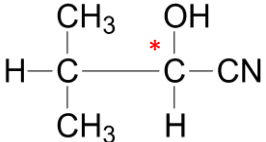
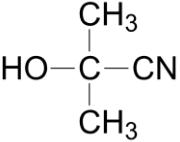
	Products obtained after elimination of H ₂ O (dehydration)
A	 no cis-trans isomerism due to two identical H atoms attached to C of the C=C bond
B	 or Either H atom from the two adjacent C atoms could be eliminated with OH, thus forming two alkenes
C	 cis-trans isomerism due to two non-identical substituents attached to each C of the C=C bond
D	 or Either H atom from the two adjacent C atoms could be eliminated with OH, thus forming two alkenes

30. **B**

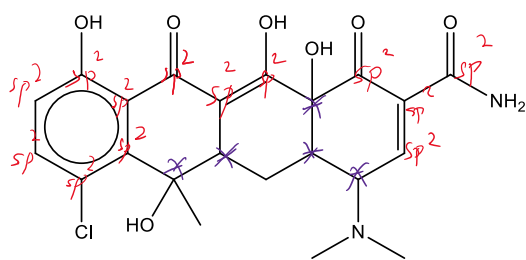
The smallest number of carbon atoms is 5.

31. **B**

Carbonyl compounds undergo nucleophilic addition with HCN

	Products obtained from reaction with HCN
A	no reaction as the compound is an ester
B	
C	 no chiral centre
D	no reaction as the compound is an alkane

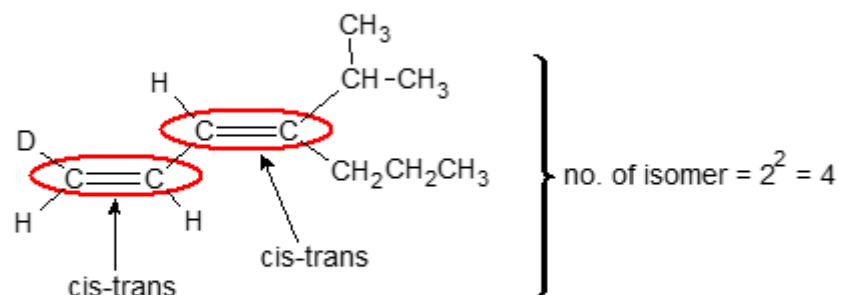
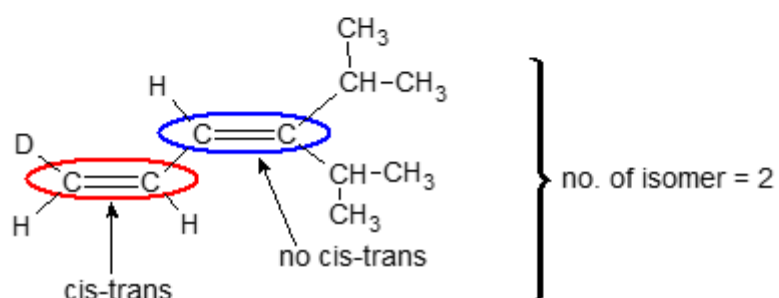
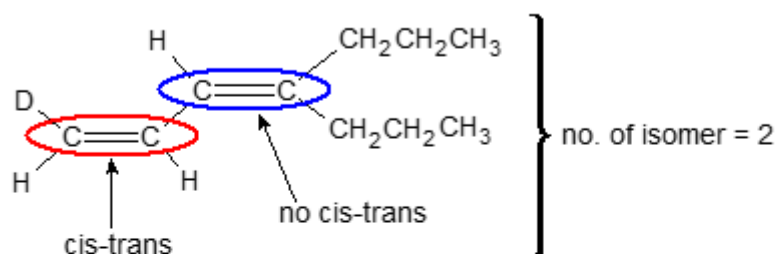
32.

D

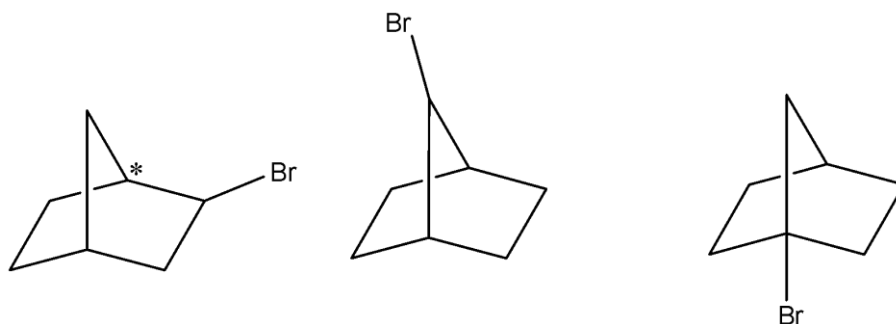
Number of chiral centres: 5

Number of sp^2 hybridised C: 13

33.

Answer: C

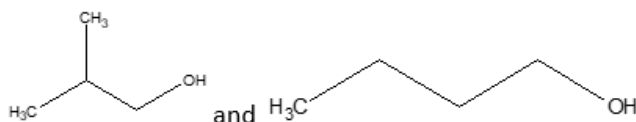
Total no. of isomers = 8

34. **B**

There are 3 structural isomers. One of them has a chiral carbon (C*) so there are 4 isomers including stereoisomers.

35. **Answer: B**

Since product **N** gives a reddish brown precipitate when reacted with Fehling's solution, an aldehyde functional group is present. Since aldehydes are formed from controlled oxidation of a primary alcohol, the possible structures of primary alcohol from $C_4H_{10}O$ are:



Therefore, there are 2 isomers.

Organic Reactions/Synthesis

36. **B**

Information

- is unaffected by hot alkaline potassium manganate(VII) $\Rightarrow$ absence of alkene, 1° & 2° alcohol
- gives hydrogen when treated with sodium $\Rightarrow$ presence of $-OH$ groups

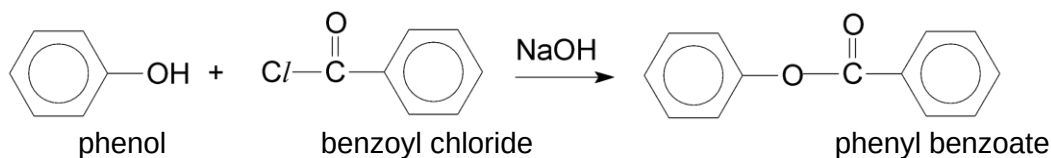
Option A: Compound is a ketone, but does not contain OH group.

Option B: Compound is a 3° alcohol.

Option C: Compound is a 1° alcohol.

Option D: Compound is a 2° alcohol.

Deduction

37. **C**

Phenyl benzoate is an ester synthesized from phenol. NaOH is added to phenol to form phenoxide ions, a better nucleophile, before it reacts with benzoyl chloride to produce phenyl benzoate.

*Note: Phenol cannot form ester with carboxylic acid.

38.

AInformationCompound **R**, $C_9H_{10}O_2$ Heated under reflux with $NaOH(aq)$ mixture then cooled and acidified with $H_2SO_4(aq)$

one product turns blue litmus solution red

another product gives a purple colouration with neutral $FeCl_3(aq)$ => phenol is presentDeduction

=> C:H ratio ~ 1:1 (Benzene ring present)

=> alkaline hydrolysis and acid base reaction

=> acidification

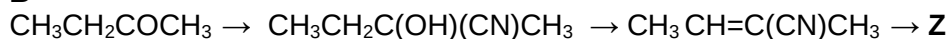
=> compound is acidic (carboxylic acid)

=> phenol is present

Hence, two products are C_6H_5OH and C_2H_5COOH . Compound **R** is an ester.

	Compound is heated under reflux with $NaOH(aq)$; mixture then cooled and acidified with $H_2SO_4(aq)$
A	$C_6H_5O\text{---}COCH_2CH_3 \rightarrow C_6H_5OH + CH_3CH_2COOH$
B	$C_6H_5CH_2O\text{---}COCH_3 \rightarrow C_6H_5CH_2OH + HO_2CCH_3$
C	$C_6H_5OCH_2COCH_3 \rightarrow$ no reaction (contain ether and ketone functional groups)
D	$C_6H_5CH_2CH_2COOH \rightarrow C_6H_5CH_2CH_2COOH$ (no hydrolysis and only 1 product)

39.

BStep I: HCN , trace amount $NaCN$, cold (Nucleophilic Addition)Step II: excess conc H_2SO_4 , heat (Elimination of H_2O)Step III: $H_2SO_4(aq)$, heat (acidic hydrolysis of CN)

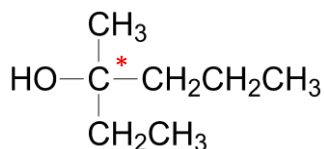
40.

CInformationAn alcohol, $C_nH_{2n+1}OH$

has a chiral carbon atom

does not react with MnO_4^- / H^+

=> 4 different substituent groups are attached to the same C atom

=> does not undergo oxidation; 3° alcohol

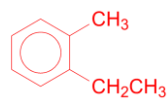
41.

C

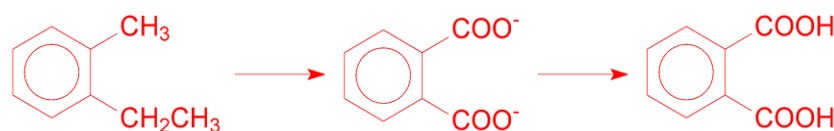
Information	Deduction
An ester Y boiled with aqueous hydrochloric acid	Acid hydrolysis
Final products include a compound $C_4H_8O_2$ which gives a pale yellow precipitate with alkaline aqueous iodine.	Oxidation (Positive tri-iodomethane test) The product contains $CH_3-\overset{\overset{O}{\parallel}}{C}-$ or $CH_3-\overset{\overset{OH}{\mid}}{\underset{\underset{H}{\mid}}{C}}-$

	Hydrolysed products
A	$CH_3OH + CH_3CH_2CH_2COOH$
B	$C_6H_5COOH + HOCH_2CH_2CH_2CHO$
C	$CH_3COOH + HOCH_2CH_2COCH_3$ (give positive tri-iodomethane test)
D	$C_6H_5COOH + HOCH(CH_3)CH_2CH_2OH$ (give positive tri-iodomethane test but have different molecular formula)

42.

D

undergoes side chain oxidation (i.e. heated under reflux with alkaline $KMnO_4$), followed by acidification (i.e. acidified with H_2SO_4).



- During side chain oxidation, all alkyl groups on benzene are oxidised to $COOH$.
- When alkaline $KMnO_4$ is used, the product formed is a salt of the carboxylic acid, instead of carboxylic acid, as it undergoes acid base reaction with the alkaline medium

43.

C

	Y	Z (If hot acidified $K_2Cr_2O_7$)	Z (If hot acidified $KMnO_4$)	Warm with alkaline aq I_2
A		no oxidation product (phenol cannot be oxidised)		No yellow ppt
B		no oxidation product (phenol cannot be oxidised)		No yellow ppt
C				Both Y and Z give yellow ppt
D				No yellow ppt for both Y and Z.

44.

D**Step I: Nitration**

The presence of the COOH group draws electron density away from the benzene ring, which makes benzene less susceptible towards electrophilic substitution. Hence, nitration must be performed at temperature above 60°C for the reaction to take place.

Step II: Reduction

The use of (1) conc HCl and (2) presence of COOH group protonates $-\text{NH}_2$ to give $-\text{NH}_3^+$. Hence, this step is not feasible.

*a follow up addition of excess NaOH (aq) is required to produce $-\text{NH}_2$

Step III: Condensation reaction

Phenylamine undergoes condensation reaction with ethanoyl chloride to form amide.

45.

C

Compound **R** could be $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ since $\text{C}_3\text{H}_7\text{Br}$ could undergo nucleophilic substitution with $\text{OH}^-(\text{aq})$ to form **R**.

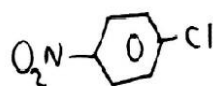
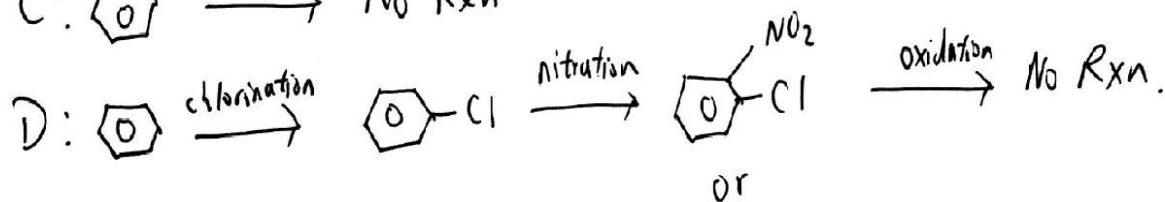
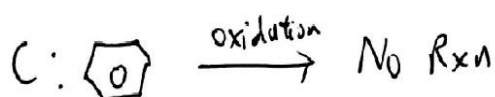
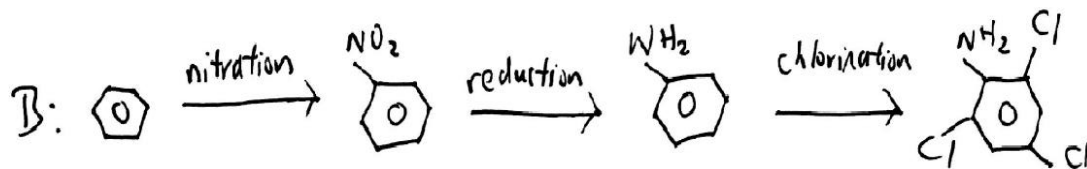
Since compound **S** has a positive reaction with Tollen's reagent, it must contain the aldehyde functional group.

Hence only choice **C** is correct, since **S** is stated as $\text{CH}_3\text{CH}_2\text{CHO}$ in choice **C**, while the other choices do not have an aldehyde functional group for **S**.

Oxidation of aldehyde with Tollen's reagent is carried out in an alkaline medium, thus the final product is RCOO^- .

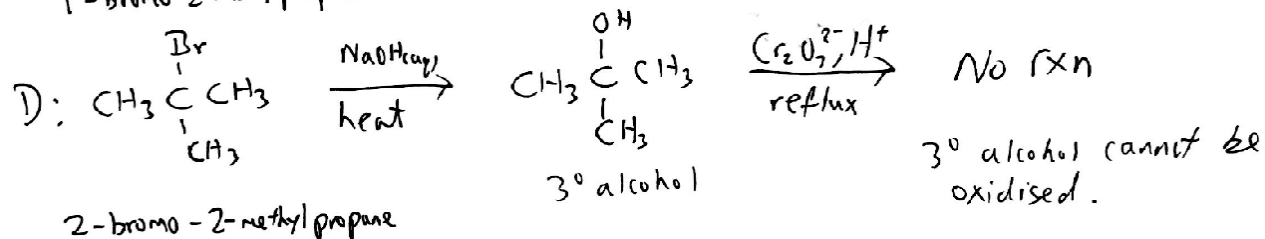
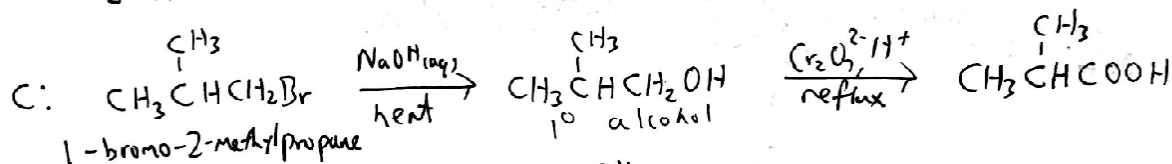
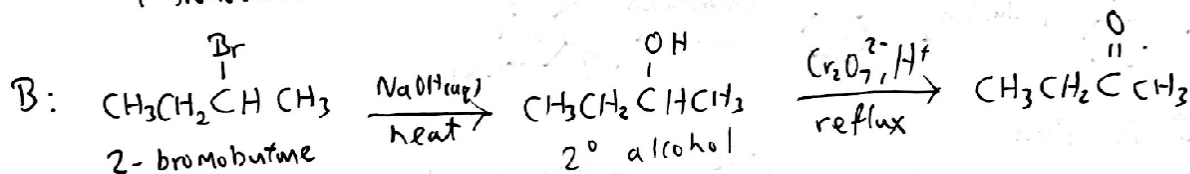
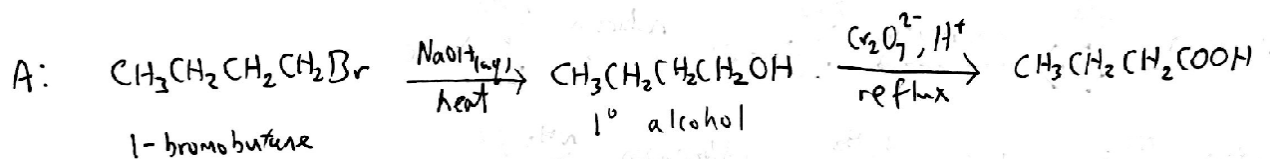
46.

A



47.

B



3° alcohol cannot be oxidised.

48.

A

For Rxn I, Since CH_3 group is not strongly ring activating, a lewis acid catalyst such as Fe or FeBr_3 is required for methylbenzene to undergo electrophilic substitution with Br_2 .

For Rxn II, $-\text{OH}$ group is strongly ring activating. Hence, no catalyst is required for electrophilic substitution reaction between phenol and Br_2 . $\text{Br}_2(\text{aq})$ will undergo multiple substitutions with phenol while Br_2 in CCl_4 will undergo monosubstitution with phenol.

For RXn III, $-\text{NH}_2$ group is strongly ring activating. Hence, no catalyst is required for electrophilic substitution reaction between phenylamine and Br_2 . $\text{Br}_2(\text{aq})$ will undergo multiple substitutions with phenylamine while Br_2 in CCl_4 will undergo monosubstitution with phenylamine.

49.

A

$\text{C}_6\text{H}_5\text{CH}_3$ is methyl benzene, it will undergo side-chain oxidation to form benzoic acid. Hence, the oxidising agent is decolourised. There is no loss of carbon atom in the oxidation process (since there is only 1 C in the side chain) hence CO_2 is not formed and no effervescence is observed.

$\text{CH}_3\text{CH}=\text{CH}_2$ is a terminal alkene. It undergoes oxidative cleavage with KMnO_4 to form carbon dioxide, explaining the decolorisation of KMnO_4 and the effervescence of CO_2 .

$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ has no functional group that can be oxidised. Hence there is no reaction with the oxidising agent.

50.

B

The compound 2-chloro-phenol has the acidic phenol functional group. Hence, it undergoes acid-base reaction with $\text{NaOH}(\text{aq})$ to form sodium phenoxide.

51.

D

Information	Deduction
When an organic compound Q was treated with phosphorous pentachloride, fumes of hydrogen chloride were evolved.	Q undergoes nucleophilic substitution with PCl_5 . Q contains either carboxylic acid group or alcohol group.
When Q warmed with alkaline aqueous iodine, a yellow ppt was formed.	Q undergoes oxidation (positive tri-iodomethane test). Hence Q has the $\text{CH}_3\text{CH}(\text{OH})-$ structure and is not a carboxylic acid.

52.

D

A: The tetracycline molecule has alcohol functional group. Hence it will undergo nucleophilic substitution with SOCl_2 .

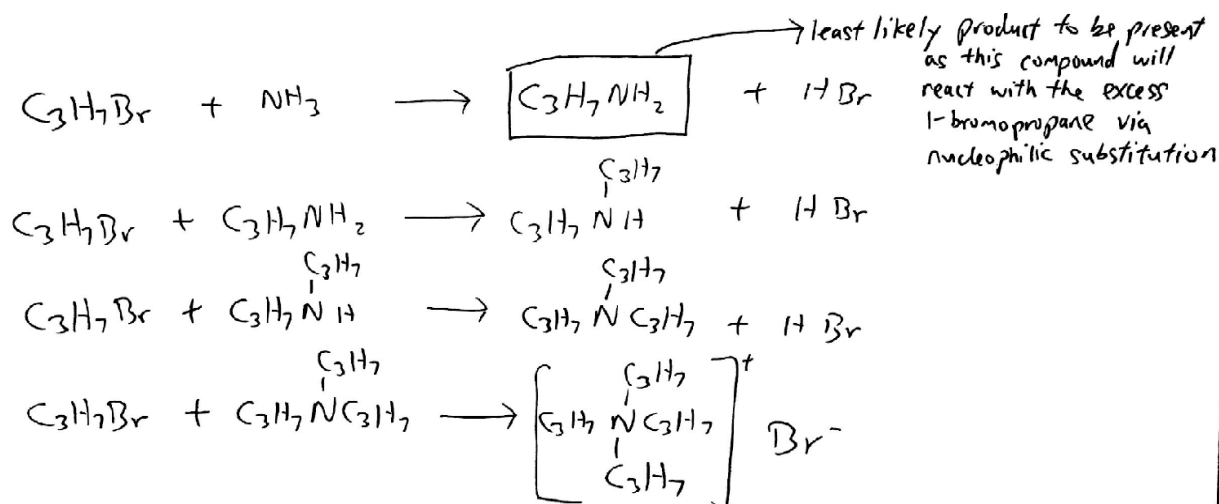
B: The tetracycline molecule does not have any carboxylic acid functional group to react with sodium carbonate. Phenol functional group is only a weak acid, not able to liberate carbon dioxide from carbonates.

C: There is one phenol group in the tetracycline molecule. However, the 2-position of the phenol group is already occupied. Hence only the 4- and 6- position are available to be substituted by Br. Hence only 2 mol of HBr will be formed from the electrophilic substitution reaction between the tetracycline molecule and aqueous bromine. There are 2 alkene groups in tetracycline, electrophilic addition with $\text{Br}_2(\text{aq})$ will also produce 2 mol of HBr. Hence a total of 4 mol of HBr is expected.

D: The tetracycline molecule contains phenol and alcohol groups which can both react with sodium metal to liberate hydrogen gas.

53.

A



54.

D

	Amine obtained from rxn of X with ammonia	Amine obtained from reduction of Y
A	$(\text{NH}_2)_2\text{CHCH}_2\text{NH}_2$	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
B	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
C	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
D	$\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$	$\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$

55.

A

The oestrone molecule has a ketone functional group, hence it can be reduced by lithium aluminium hydride to form secondary alcohol.

56.

C

A: Compound P exhibits cis-trans isomerism as it has different groups attached to each of the doubly bonded carbon atoms; Compounds Q and R exhibit optical isomerism due to the presence of chiral carbons. Both cis-trans isomerism and optical isomerism are stereoisomerism. Hence all three compounds exhibit stereoisomerism.

B: Compound P contains 2 alkene groups. For the terminal alkene group, CO_2 is formed when it undergoes oxidative cleavage. For the other alkene group ($=\text{CHCHO}$), ethanedioic acid is formed which will be further oxidised to CO_2 and H_2O . Hence only 1 organic product is formed from the oxidative cleavage of both alkene groups of compound P.

C: R contains alcohol functional group, while P and Q do not. Phosphorus pentachloride undergoes nucleophilic substitution with alcohol to form halogenoalkane and HCl gas which is a dense white fume.

D: While the aldehyde group in P can be reduced to the primary alcohol group in R with lithium aluminium hydride, the alkene group in P cannot be reduced to the alkane group in R. H_2/Pt catalyst is required to reduce alkene to alkane.

57.

C

A: Potassium manganate (VII) can cause oxidative cleavage of the C=C functional group of the molecule

B: Hydrogen with platinum catalyst will reduce the C=C functional group to alkane.

C: Alkaline Ag^+ ammonia complex is Tollen's Reagent which reacts only with aldehyde functional groups. This molecule does not have aldehyde functional group.

D: Hot aqueous sodium hydroxide will hydrolyse the amide functional group in this molecule.

58.

C

(i) Decolourise aqueous bromine --- presence of either alkene group, phenol or phenylamine groups

(ii) Forms yellow ppt with alkaline aqueous iodine --- presence of $-\text{C}=\text{O}(\text{CH}_3)$ or $-\text{CH}(\text{OH})(\text{CH}_3)$ groups.

(iii) liberates one mole of H_2 gas when two moles of sodium is added---- Presence of two protonic H atoms (found in $-\text{OH}$ and $-\text{COOH}$ groups) per molecule.

59.

B

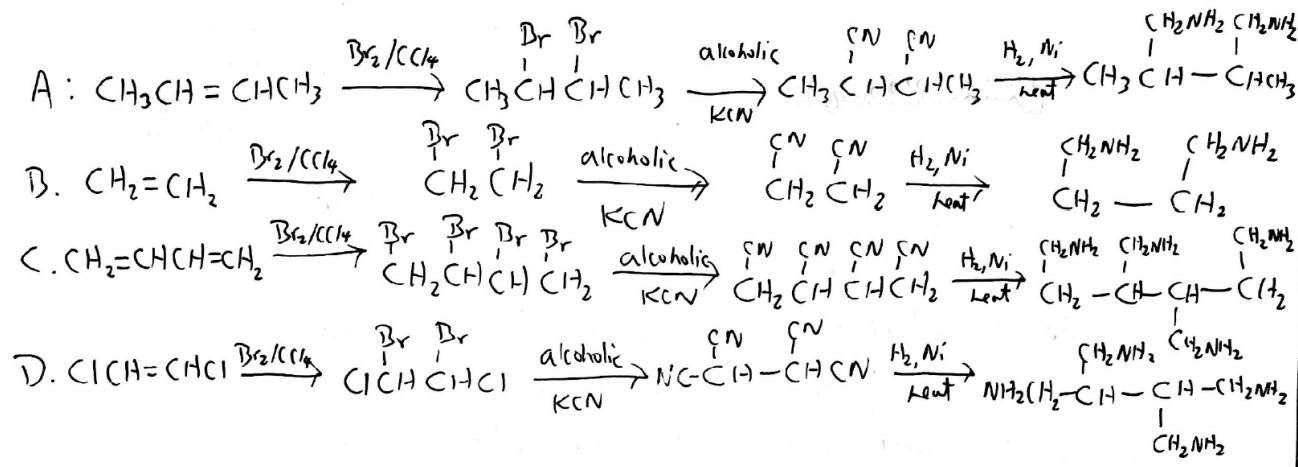
A: There are 2 chiral carbons (both adjacent to each of the N atom) and no plane of symmetry in the molecule. Hence the molecule is optically active.

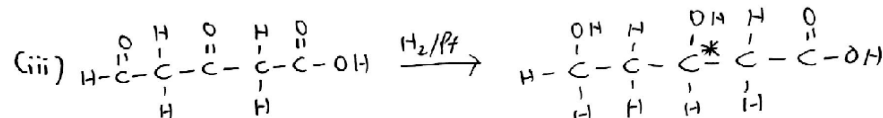
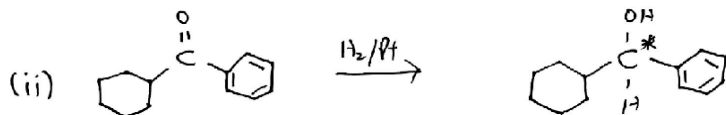
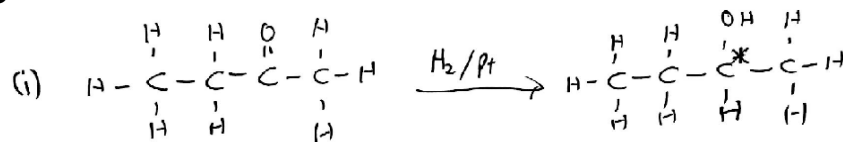
B: The molecule has an acidic carboxylic acid group as well as a basic amine group. Hence it can exist as zwitterion.

C: There is one ester group and one amide group in the molecule. When subjected to alkaline hydrolysis with sodium hydroxide, the molecule breaks up into 3 separate molecules.

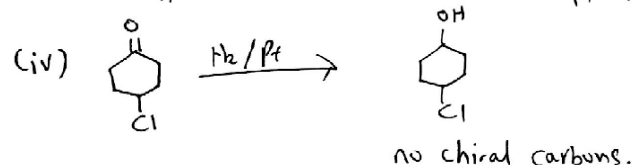
D: There is no alkene, phenol or phenylamine functional groups to decolourise aqueous bromine in the absence of light.

60.

B

61. **C**

Note: H_2/Pt do not reduce $-COOH$ group.

62. **D**

"reaction proceeded faster when the substituent **G** is a methyl group as compared to a bromine group" suggests that reaction is faster with an electron-donating group.

In the options, Cl and NO_2 are electron-withdrawing groups. H has no effect. $-OCH_2CH_3$ is an electron-donating group as the lone pair of O can be delocalised into the benzene.

63. **C**

"does **not** decolourise hot acidified $KMnO_4(aq)$ " means that none of the functional groups can be oxidised by $KMnO_4$.

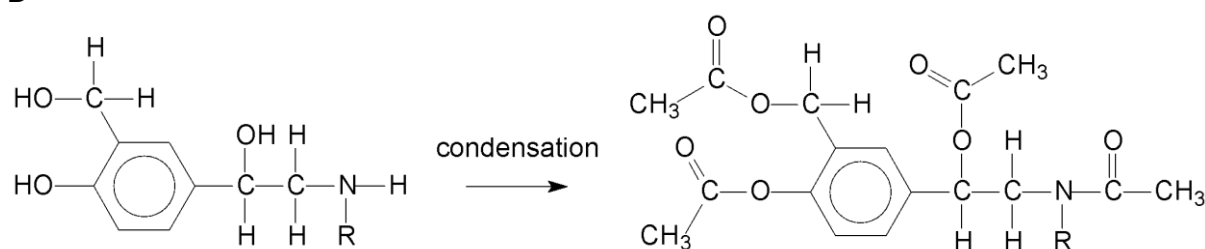
"gives a salt when reacted with $NaOH(aq)$ " means that compound contains acidic CO_2H or phenol groups.

Hot acidified $KMnO_4$ will first hydrolyse the ester (option **A**: $CH_3CO_2CH_2CO_2H$) into CH_3CO_2H and $HOCH_2CO_2H$. $HOCH_2CO_2H$ has a primary alcohol that can be oxidised by $KMnO_4$. Hence **A** is wrong.

$KMnO_4$ will oxidise the primary alcohol (**B**: $CH_2(OH)COCH_2CO_2H$). Hence **B** is wrong.

$KMnO_4$ will NOT oxidise the tertiary alcohol (**C**: $(CH_3)_2C(OH)CH_2COOH$). Acidic CO_2H is also present. Hence answer is **C**.

$KMnO_4$ can oxidise the methyl side-chain in **D**. Hence **D** is wrong.

64. **D**

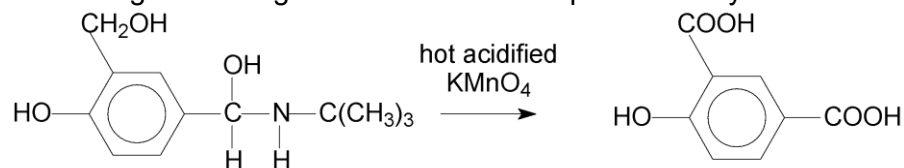
$CH_3COC/$ (acyl chloride) can react with alcohol, phenol and amine to form esters and amides. Hence 4 moles of ethanoyl chloride is needed.

65.

D

A is wrong. There is only 1 basic amine group, hence 1 mole of Salbutamol reacts with only 1 mole of dilute HNO_3 .

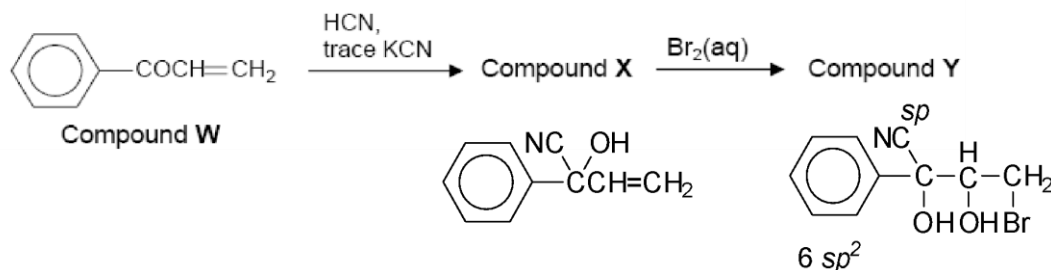
B is wrong as Fehling's solution tests for aliphatic aldehyde.



C is wrong as none of the OH is adjacent to a C-H, hence dehydration does not occur.

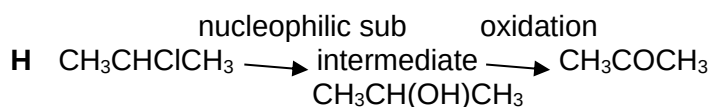
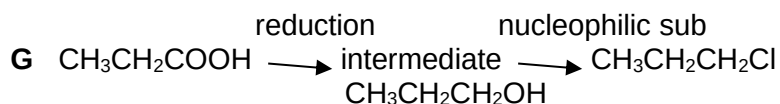
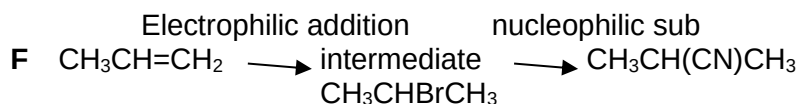
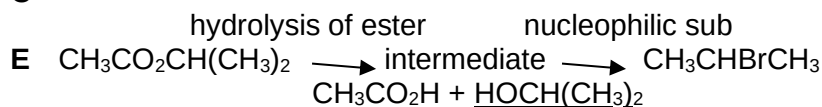
D is correct as bromine solution can react with phenol.

66.

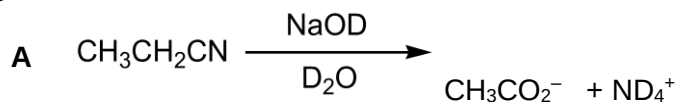
C

The remaining carbons are sp^3 hybridised, hence answer is **C**.

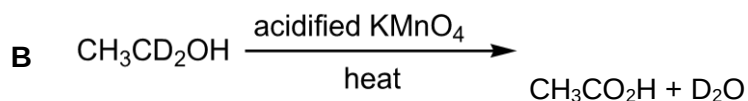
67.

C

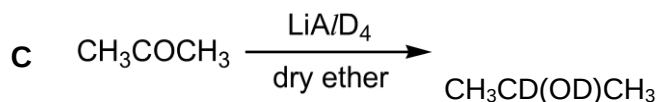
68.

C

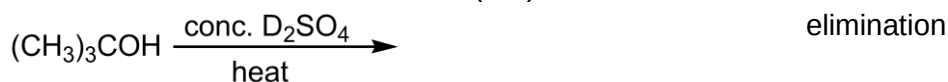
alkaline hydrolysis of nitrile



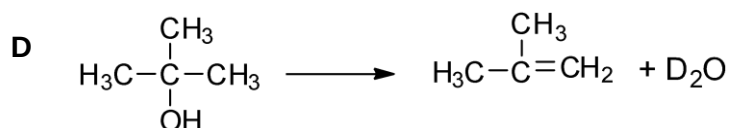
Oxidation of primary alcohol



reduction



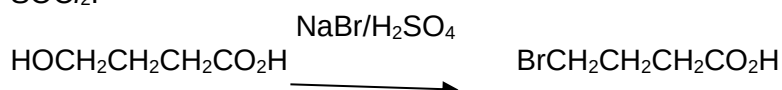
elimination



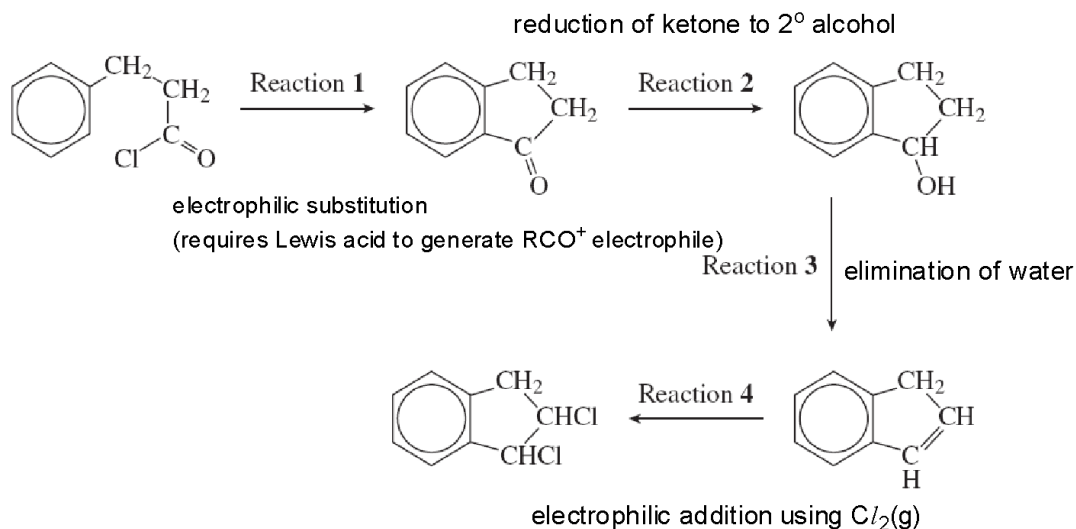
69.

BNaBr and H₂SO₄ generates HBr(g) *in situ*. (in the reaction mixture)

HBr reacts with alcohols (not carboxylic acid) via nucleophilic substitution.

Halogenation reagents that can react with both alcohols and carboxylic acids are PCl₅, PCl₃, PBr₃, SOCl₂.

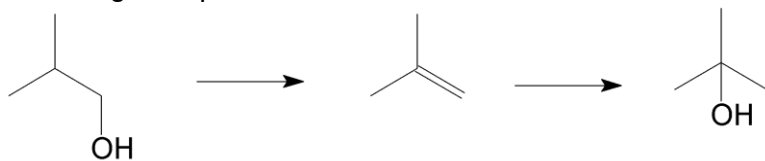
70.

D

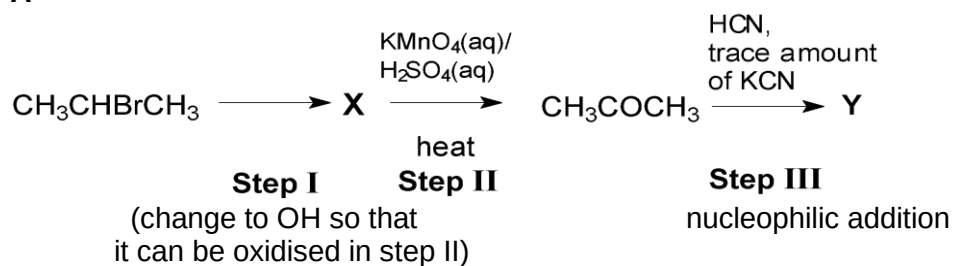
71.

C

To change the position of OH, a series of elimination and addition of water can be used



72.

A

Take note that alcoholic OH^- is used for elimination of HX whereas aqueous OH^- is used for nucleophilic substitution.

73.

D

3 moles of $\text{Br}_2(\text{aq})$ are needed as a max of 3 Br can be substituted into benzene.

1 mole of PCl_5 is needed as only the alcohol will react with PCl_5 .

Only 2 moles of NaOH are needed to react with the 2 acidic phenolic groups. No reaction with the neutral alcohol.

5 moles of acyl chloride reacts with phenol, alcohol and amine via condensation.

74.

B

Compound X

- can react with 2,4-dinitrophenylhydrazine (has carbonyl group)
- does not react with Fehling's solution (has ketone or benzaldehyde)
- can be oxidized to benzene-1,4-dicarboxylic acid (has alkyl, primary alcohol or aldehyde at side-chain)

A is wrong as phenol cannot be oxidised to benzoic acid.

C is wrong as $-\text{CBr}_2-$ does not contain any H for side-chain oxidation to occur.

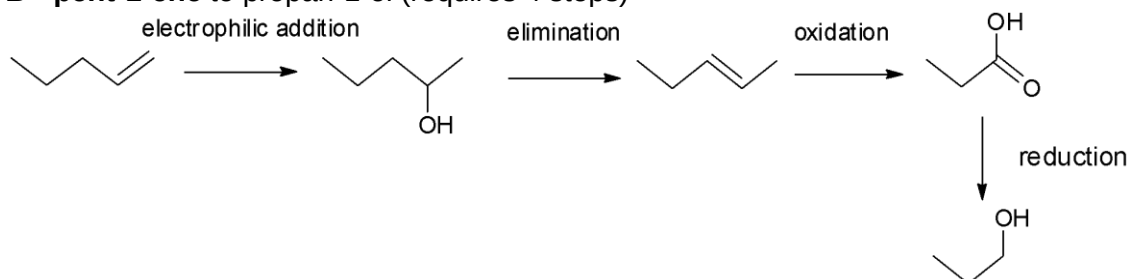
D is wrong as $-\text{OCO}-$ ester group will be hydrolysed to phenol and RCO_2H when hot acidified KMnO_4 is used. Phenol will not be oxidised any further.

75.

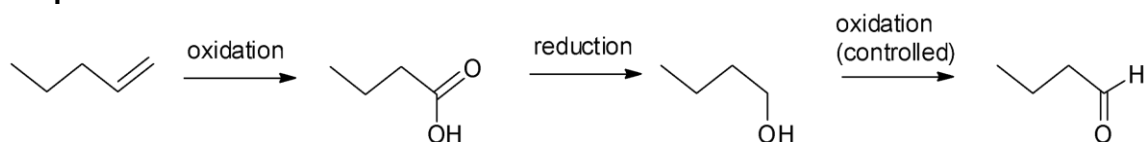
B

A pent-1-ene to pent-2-ene (requires electrophilic addition of H_2O or HX , followed by elimination of H_2O or HX to change the position of $\text{C}=\text{C}$)

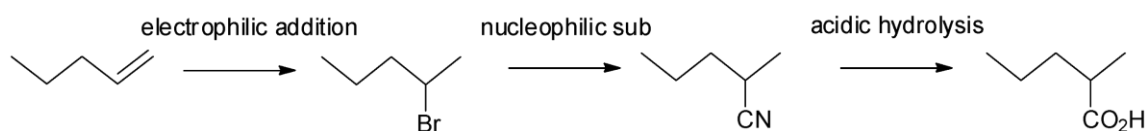
B pent-1-ene to propan-1-ol (requires 4 steps)



C pent-1-ene to butanal



D pent-1-ene to 2-methylpentanoic acid



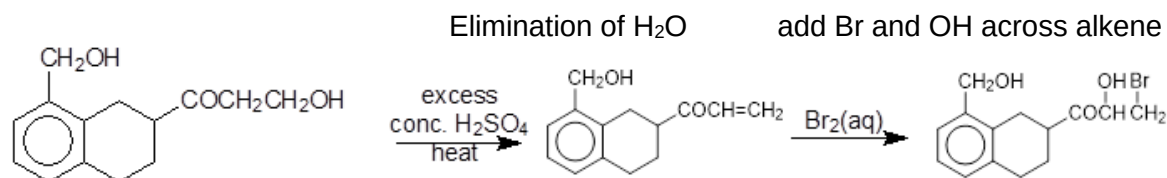
76. **A**

A $\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{Br}_2 \rightarrow \text{DBCP}$ (1,2-dibromo-3-chloropropane) the 2 Br will be added across the first two carbons and only 1 product is formed, thus ensuring high yield.

B $\text{CH}_3\text{CHBrCH}_2\text{Br} + \text{Cl}_2 \rightarrow \text{DBCP} + \text{HCl}$ (free radical substitution results in multiple products, hence it is not recommended to be used in synthesis)

C $\text{CH}_2=\text{CHCHBr}_2 + \text{HCl} \rightarrow$ will form $\text{CH}_3\text{CHClCHBr}_2$, 1,1-dibromo-3-chloropropane, instead

D $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + 2\text{Br}_2 \rightarrow \text{DBCP} + \text{HBr}$ (same reason as **B**)

77. **D**

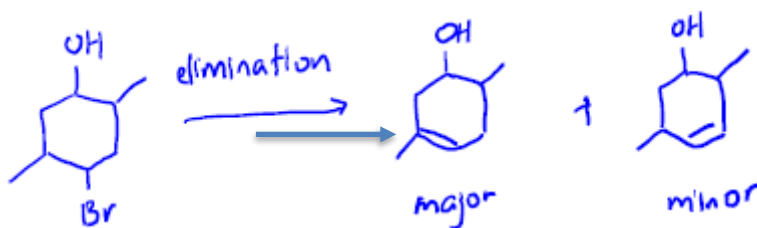
No Br will be substituted into benzene as phenol and phenylamine are not present.

78. **C**

To prepare ethene from ethanol, we must do elimination using excess conc H_2SO_4 (reagent **Y**) and heat. To remove the unreacted conc acid, NaOH (reagent **Z**) can be added to neutralise it.

79. **C**

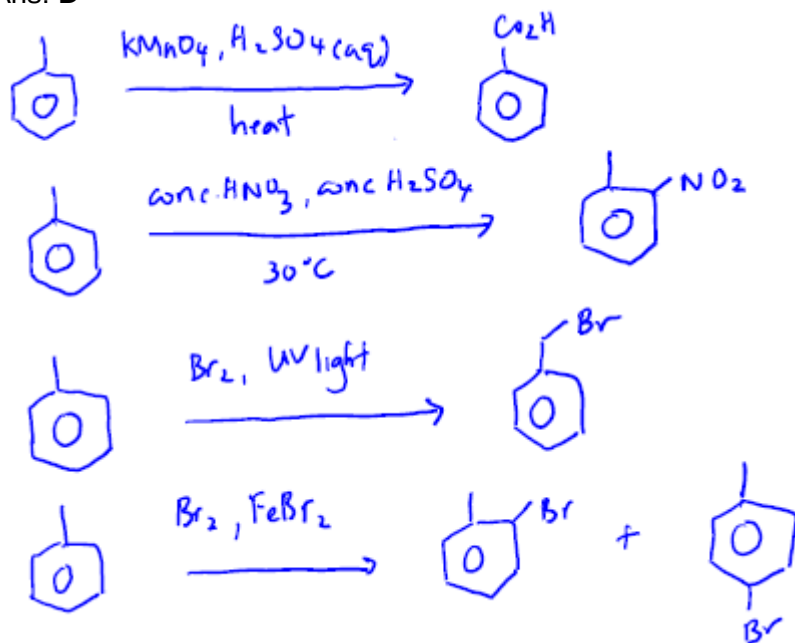
X will undergoes elimination of HBr with ethanolic KOH to form an **alkene** functional group. According to Zaitsev's rule, the more substituted alkene will be more stable, hence the major product.



Note: The elimination of water occurs if reacted with excess concentrated H_2SO_4 with heating.

80.

Ans: D



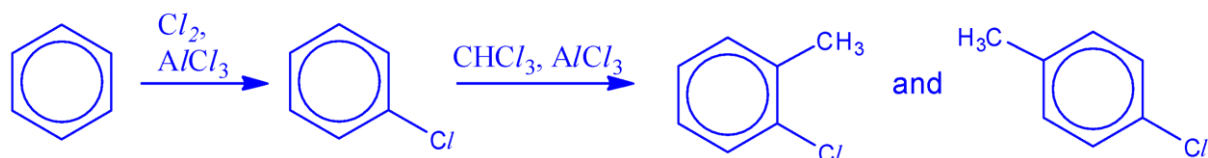
81.

Hence, 3-bromomethylbenzene cannot be obtained in 1 step from methylbenzene.

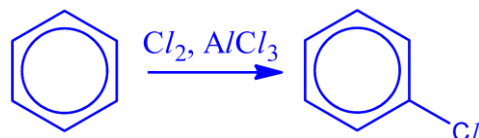
C

In this synthesis, we need to substitute $-\text{CH}_3$ (which is subsequently oxidised to $-\text{CO}_2\text{H}$) and $-\text{Cl}$ onto the benzene ring. Since both $-\text{CH}_3$ and $-\text{Cl}$ are 2,4-directing, but we want a 1,3-disubstituted product, we need to get $-\text{CH}_3$ on the ring first so that we can oxidise it to $-\text{CO}_2\text{H}$, which is 3-directing.

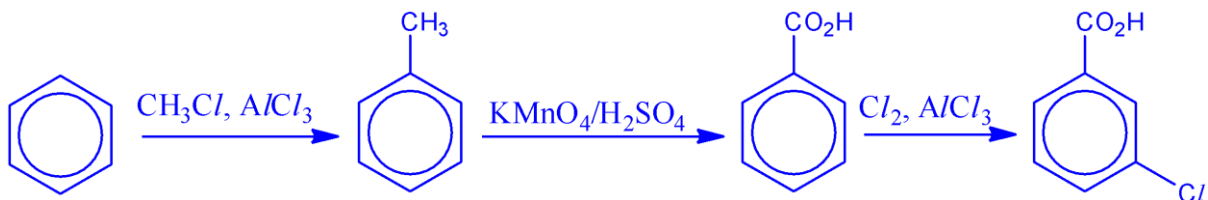
Option A: $-\text{CH}_3$ is substituted on 2- and 4-positions instead of the 3-position.



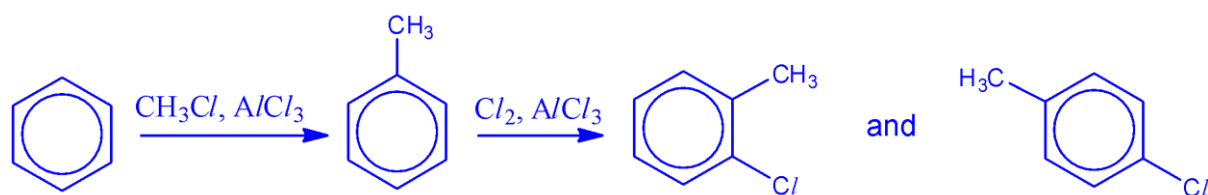
Option B: No alkyl side-chain for KMnO_4 to oxidise in Step 2.



Option C:



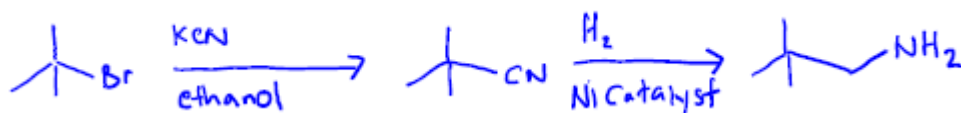
Option D: $-\text{Cl}$ is substituted on 2- and 4-positions instead of the 3-position.



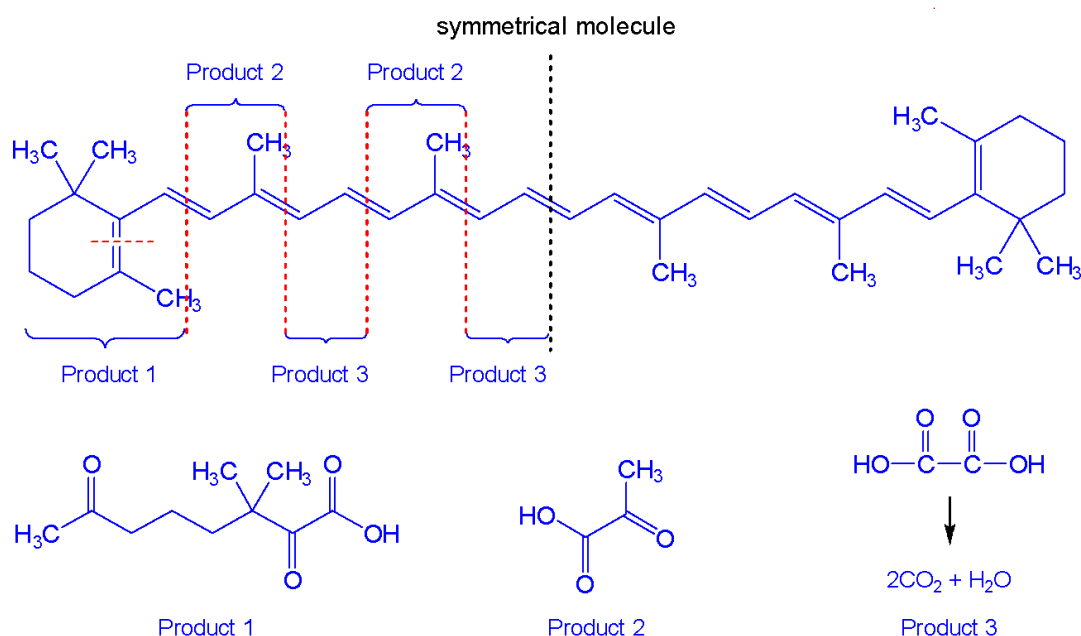
82.

B

E undergoes **nucleophilic substitution** to form **F** (contains a CN group), which subsequently is being **reduced** to give a primary amine.



83.

A

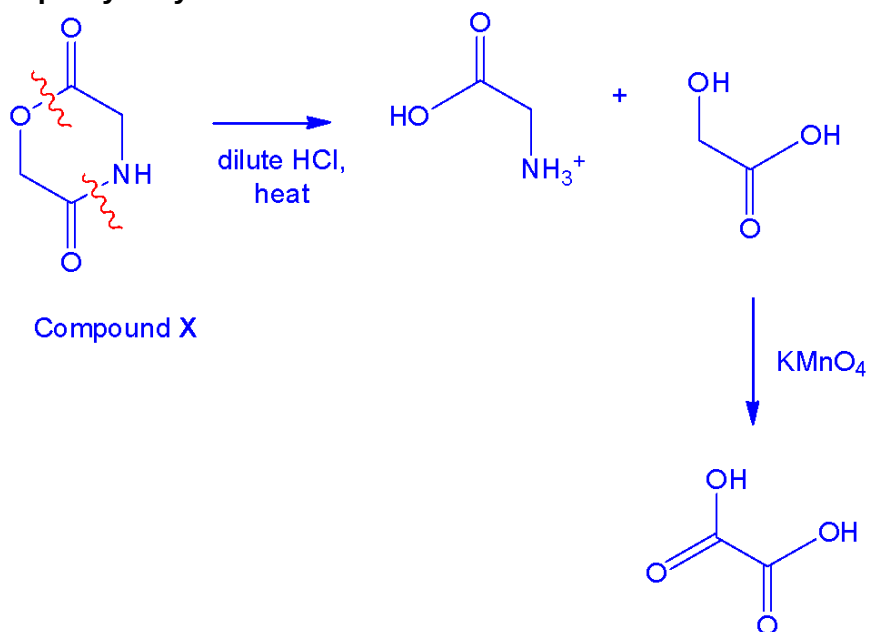
Since the molecule is symmetrical, there are only 2 different products that contained ketone groups.

84.

A

- Statement 1: True. Only an alkene can decolourise Br_2 in CCl_4 via electrophilic addition. Thus, both compounds **I** and **III** will not decolourise Br_2 .
- Statement 2: False. Compound **I** will not decolourise purple KMnO_4 at room temp.
- Statement 3: False. The alkyl side-chain of compound **III** will be able to undergo free radical substitution with Cl_2 gas when exposed to uv light.
- Statement 4: True. Compound **III** requires FeBr_3 catalyst for electrophilic substitution to occur.

85.

B**Concept: hydrolysis of amides and esters**

ethanedioic acid undergoes further oxidation to give CO₂ and H₂O

86.

A

- 1 It dissolves in water to give a neutral solution. **False; Binapacryl is not soluble in water.**
- 2 It is inert towards acidified potassium dichromate solution. **True; acidified K₂Cr₂O₇ is not strong enough to oxidise the alkyl side-chain.**
- 3 It decolourises aqueous bromine to form a white precipitate. **False; phenolic group in Binapacryl is already 2, 4 substituted. Hence will not be able to undergo further electrophilic substitution with aq. Br₂.**
- 4 It reacts with ethanoic acid in the presence of concentrated sulphuric acid to form an ester. **False; phenol and ethanoic acid are both weak acids; no reaction between both compounds. To form ester with phenol, acyl chloride is required instead.**

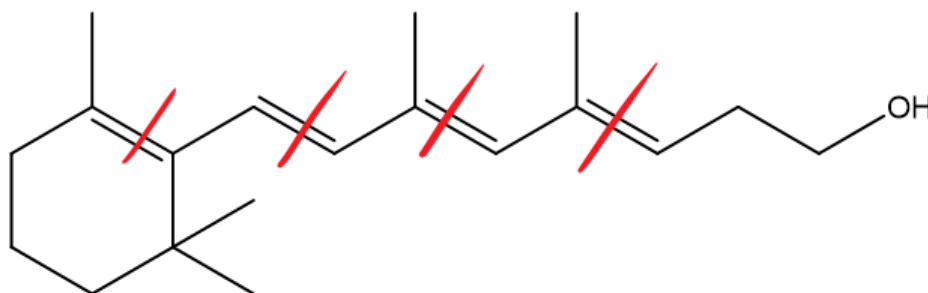
87.

A

A: HCl (white fumes) is formed when the alcohol reacts with ethanoyl chloride.

B: is wrong as C=C is electron rich hence does not undergo reaction (reduction) with hydride H^- from LiAlH_4 .

C: is wrong since NO CO_2 produced due to absence of terminal alkane and absence of ethanedioic acid produced that can be further oxidised to CO_2 .



D: 1 mol of Vitamin A produces 0.5 mol of H_2 and that is $22.7/2 = 11.35 \text{ dm}^3$ at stp.

88.

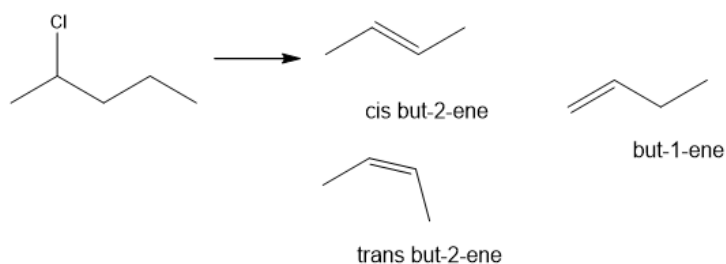
D

Option 1 is wrong since $\text{CH}_3\text{CH}_2\text{CHClCH}_3$ undergoes $\text{S}_{\text{N}}2$ nucleophilic to give an optically active product, $\text{CH}_3\text{CH}_2\text{CH(OH)CH}_3$. The product would be a racemic mixture if it underwent $\text{S}_{\text{N}}1$ mechanism.

Option 2 is correct as $\text{CH}_3\text{CH}_2\text{CH(OH)CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$ are functional group isomers.

Option 3 is correct as C–Br bond is weaker than C–Cl bond and so rate of substitution will increase when the sample is 2–bromobutane.

Option 4 is correct as $\text{CH}_3\text{CH}_2\text{CH(OH)CH}_3$ undergoes elimination with conc H_2SO_4 to give but-1-ene, cis-but-2-ene and trans-but-2-ene.



89.

Ans: D

Option A is wrong since the intermediate $\text{CH}_3\text{CH}_2\text{CH}(\text{CN})\text{O}^-$ has a tetrahedral shape.

Option B is wrong since a racemic mixture of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$ would be obtained, effect on the plane polarised light by each enantiomer is equal in magnitude but opposite thus net zero optical activity.

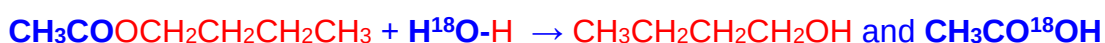
Option C is wrong since there are more $-\text{R}$ groups surrounding the carbonyl C in propane, making the C less electron deficient and also hindering the attack of the nucleophile. Hence, the rate should be slower.

Option D is correct due to nucleophilic substitution where the Cl is substituted by CN to give the same product. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$

90.

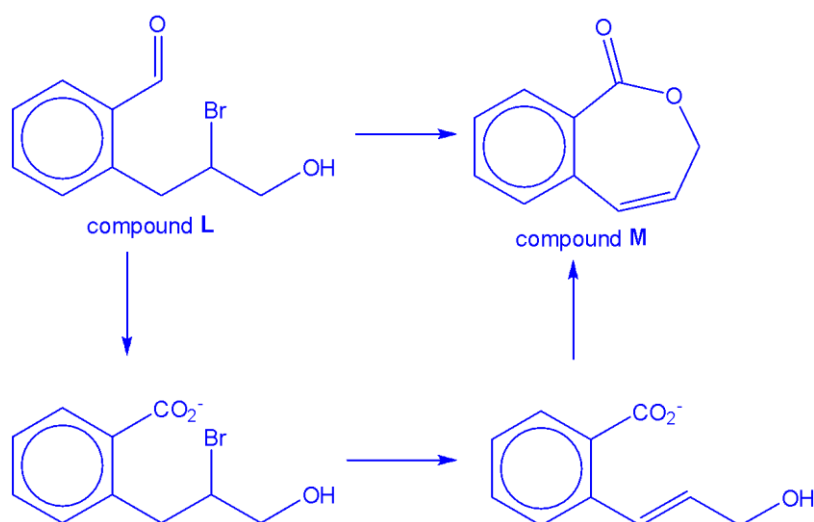
A

Butyl ethanoate is formed from butanol and ethanoic acid



Lone pair on O of H_2O reacts with the acyl C of ester.

91.

Ans: C

92.

Ans: C

1. Acid chloride reacts with phenol and alcohol to form ester and amine to form amide. So *Aureomycin* should react with 6 instead of 5 moles of acid chloride.
2. Alkenes and ketones can be reduced by hydrogen gas to form alkane and secondary alcohol respectively.
3. HBr(g) can react with the alkene via electrophilic addition, the aliphatic alcohol to form RBr via nucleophilic substitution, and both amine functional groups in an acid base reaction.

93.

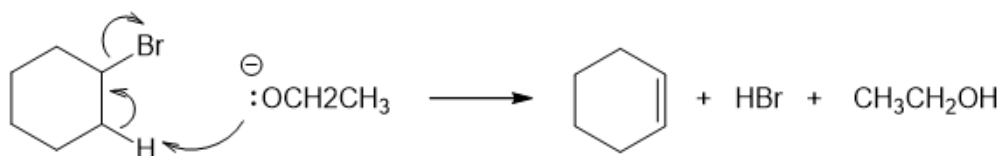
Answer: C

- A** Without UV light, Br_2 , (halogen) are electrophiles therefore can only react with electron rich C such as alkene and benzene. C attached to electronegative O of the OH group is partial positive, hence cannot react with Br_2 .

Substitution of OH with Br requires HBr (g) or PBr_3 , anhydrous as the C-O is strong and difficult to break.

- B** Br attached to $\text{C}=\text{C}$ is unreactive towards nucleophilic substitution as the p orbital on Br overlaps with the π orbital of $\text{C}=\text{C}$, resulting in partial double bond character for the carbon-bromine bond which requires more energy to break.
- C** Elimination of HBr can take place in presence of a strong base in alcoholic medium.

$\text{CH}_3\text{CH}_2\text{O}^-$ is a stronger base than OH^- since the ethyl group is electron donating which intensify the negative charge on oxygen. Thus it is able to abstract the H atom on the carbon next to carbon attached to Br.



Na^+ is a spectator ion.

- D** PCl_5 reacts with H_2O instead of COOH group since water is present as solvent.
 $\text{PCl}_5 + \text{H}_2\text{O} \rightarrow 5\text{HCl} + \text{H}_3\text{PO}_4$

Anhydrous PCl_5 should be used for this reaction to take place.

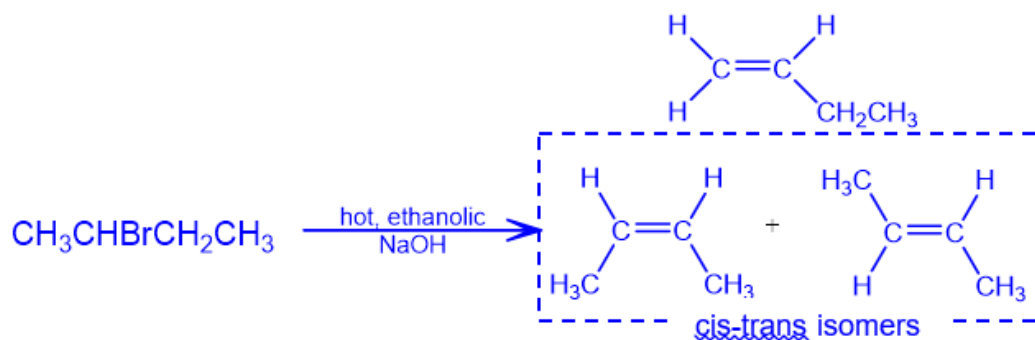
94.

Answer: B

Hot NaOH in ethanolic medium, thus elimination predominates over nucleophilic substitution.

Alcohol is formed as a minor product as **nucleophilic substitution** can still take place. Hence, statement 1 is correct.

During **elimination**, HBr can be eliminated from carbons 1 & 2, or carbons 2 & 3, to give three products, among which there is a pair of cis-trans isomers.



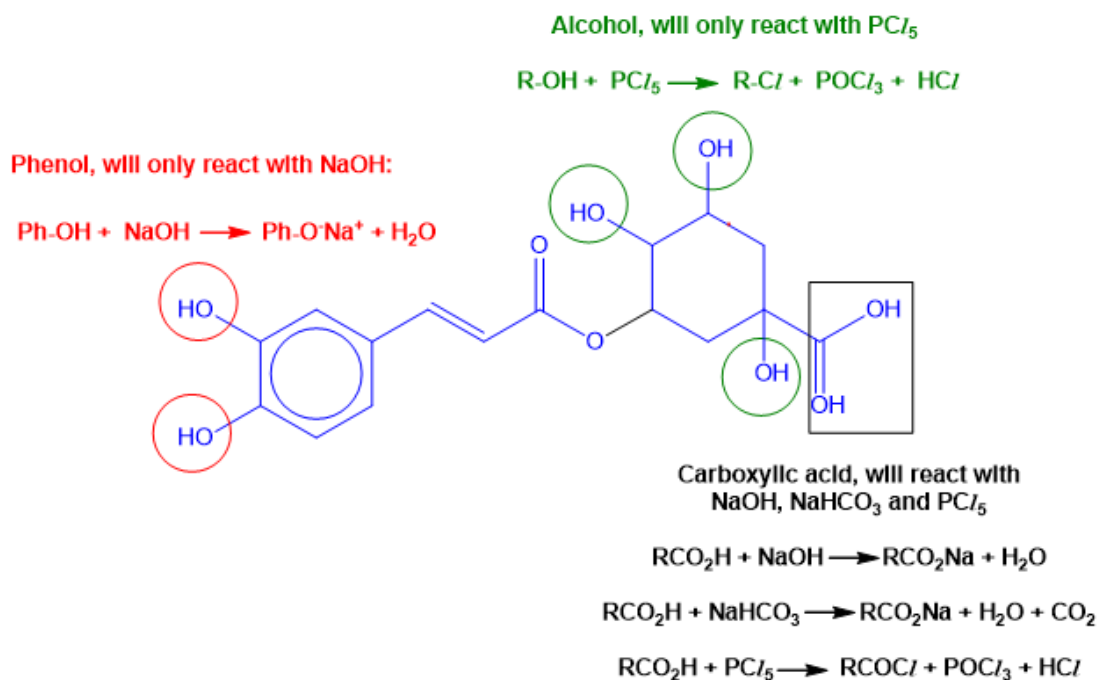
Hence statement 3 is correct.

Do not confuse this reaction with the nucleophilic substitution of Br by OH^- , which takes place preferably under aqueous conditions instead of ethanolic conditions.

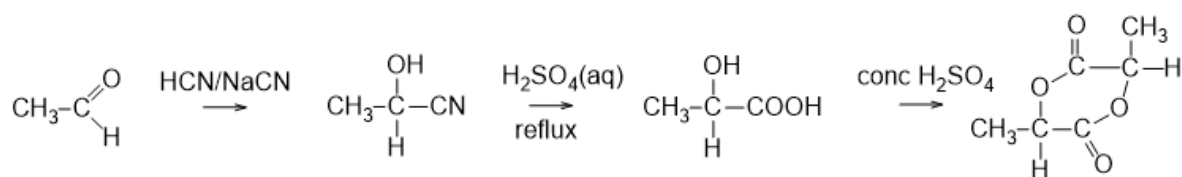
95.

Answer: D**Note:**

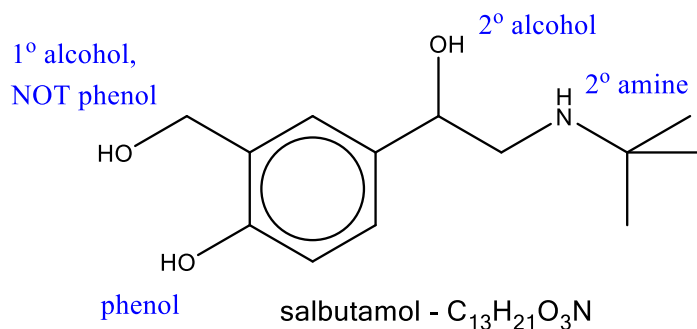
- NaOH(aq) will react with phenols and carboxylic acids only.
- NaHCO₃(aq) will react with carboxylic acids only.
- PCl₅(s) will react with alcohols and carboxylic acids only.



96.

Answer: BMolecular formula is C₆H₈O₄Empirical formula of product R is C₃H₄O₂

97. D



A – alcohols and the phenol react with acyl chlorides to form esters, while the amine reacts to form an amide.

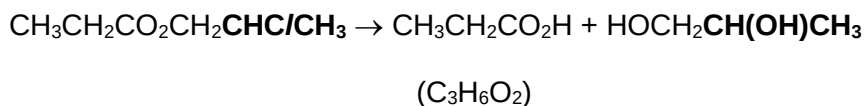
B – the 1° and 2° alcohol can be oxidized to form a carboxylic acid and ketone respectively.

C – both alcohols and phenol react with Na(s)

D – only phenol reacts with NaOH(aq)

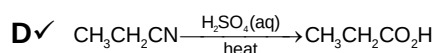
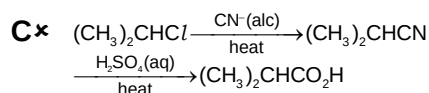
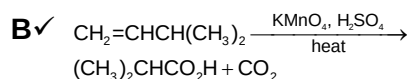
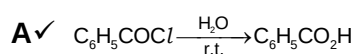
98. D

- When boiled with aq. NaOH, hydrolysis of ester and nucleophilic substitution of chloroalkane occurred.



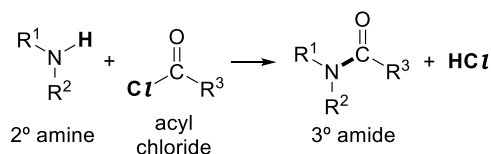
- The alcohol formed has CH₃CH(OH)– group and so, gives a positive iodoform test (yellow precipitate of CHI₃ formed).

99. C



100. A

Z is a 3° amide which can only be made from an acyl chloride and a 2° amine:



Organic Reaction Mechanism

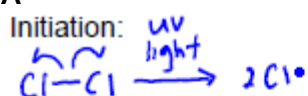
101.

B

The hydrogen in benzene is substituted by Cl atom, this is an electrophilic substitution reaction.

102.

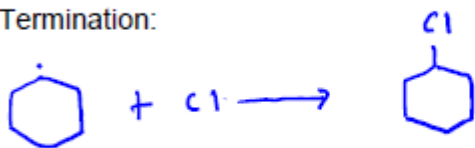
A



Propagation:



Termination:



Reaction in option B does not occur as it is more energetically favourable to form alkyl radical than the H radical.

Reaction in option C is a termination step while that of option D is the initiation step.

103.

D

Step I: The S atom in ClSO_3H is highly electron deficient, hence acts as an electrophile to attack benzene and substitute H atom. Thus, benzene undergoes electrophilic substitution.

Step II: The electronegative $-\text{Cl}$ is being substituted by $-\text{NH}_2$, so this is a nucleophilic substitution as the electron deficient C atom of $\text{C}-\text{Cl}$ is being attacked by nucleophile NH_3 .

Step III: $-\text{CH}_3$ group is being oxidised to $-\text{CO}_2\text{H}$

104.

D

NH_3 acts as a nucleophile and uses its lone pair of electrons on N to attack the electron deficient C (attached to I) in $\text{C}_2\text{H}_5\text{I}$, hence I is substituted and lost as I^- .

Mechanism involved is nucleophilic substitution.

105.

A

First step involved H^- substituting OC_2H_5 to give $^-\text{OC}_2\text{H}_5$, this is a nucleophilic acyl substitution.

Second step involved H^- attacking the carbonyl carbon to break the π bond in $\text{C}=\text{O}$ and form a σ bond with the carbon to give an alkoxide. This is a nucleophilic addition reaction.

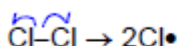
Third step involved the transfer of H^+ from water molecules to the 2 alkoxides (RO^-) to form alcohol, hence this is an acid-base reaction.

Condensation is NOT involved in this reduction process.

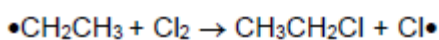
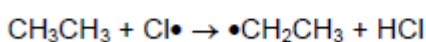
106.

B

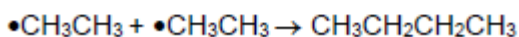
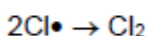
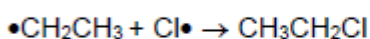
Initiation:



Propagation:



Termination:



Homolytic fission and bond formation occur in the propagation step as well, hence option **A** and **C** are incorrect.

The product chloroethane is formed in the propagation and termination step, hence option **D** is incorrect.

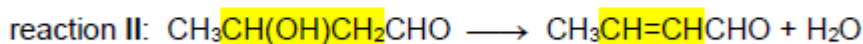
Small quantities of butane are formed due to the collision of two alkyl radical in the termination step. Hence **B** is correct.

107.

A

ethanal

aldol



aldol

reaction I: The aldehyde functional group (highlighted in yellow) undergoes **addition** to become an alcohol.

reaction II: The alcohol functional group (highlighted in yellow) then undergoes **elimination** to form an alkene.

108.

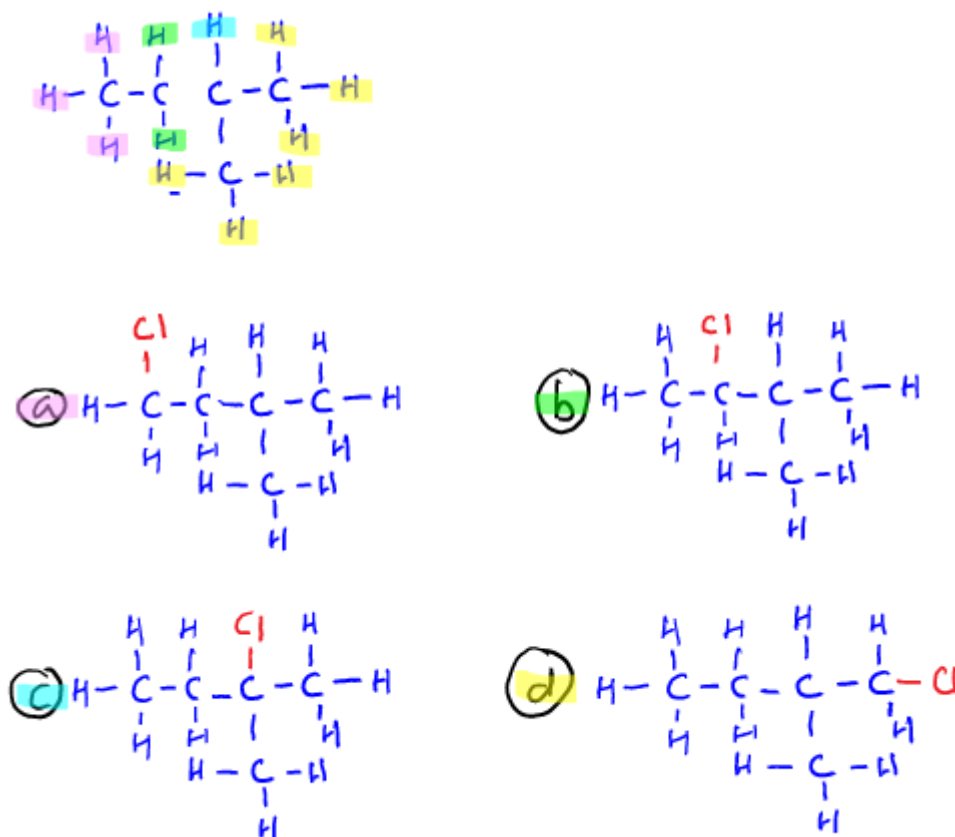
B

Compare bond energy values quoted from Data Booklet

Bond	Energy / kJ mol ⁻¹
H-Cl	431
Cl-Cl	244
H-H	436
C-H	410

Since Cl-Cl is the weakest bond, it will be the easiest initiating step.

109.

B

There are 4 possible monosubstituted products.

Based on the number of hydrogen atoms (colour-coded) that can be substituted to give the respective product, the ratio of product a, b, c and d is 3:2:1:6.

Hence the ratio of the two compounds with the highest yield, which is a and d, is 3:6 (i.e. 1:2).

110.

A

Based on the number of hydrogen atoms (colour-coded) that can be substituted to give the respective product, the ratio of product

1-chloropentane : 2-chloropentane : 3-chloropentane

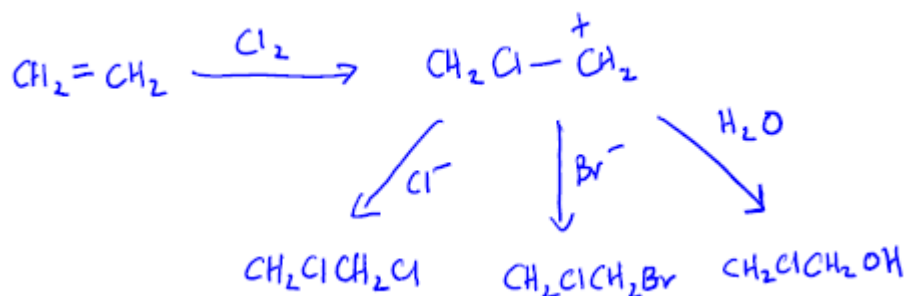


6 : 4 : 2

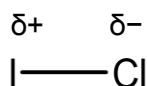
4 simplest ratio is 3:2:1.

111. **D**
The central carbon has only 3 valence electrons (trivalent), it is short of 1 electron and is positively charged.
All 3 electrons are used in bond formation, hence the carbon is surrounded by 6 six outermost electrons and does not contain an unpaired electron.

112. **C**
 Cl_2 is the only electrophile that reacts with ethene, hence the product will contain Cl atom. The molecule in option C will not be formed.



113. **B**
In the $\text{I}-\text{Cl}$, Cl is more electronegative than I. Hence, the I have a partial positive charge while the Cl will have a partial negative charge.



The subsequent electrophile generated will be an I^+ and will be substituted into the benzene ring. A Cl^+ will not be formed.

114. **B**
To generate the strong electrophile NO_2^+ , H_2SO_4 will protonate HNO_3 in the following reaction.
 $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$
 $\text{H}_2\text{NO}_3^+ \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^+$
 Thus, the electrophile is generated for the electrophilic substitution.

115. **D**
 AlCl_3 is the catalyst used to react with CH_3Cl and generate the strong electrophile CH_3^+ .
 $\text{AlCl}_3 + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{AlCl}_4^-$

116. **B**
The arrow must start from a source of electron e.g lone pair or bond and the arrow head must end at on an atom that is electron deficient e.g having a positive charge or a partial positive charge.

117. **B**
In both steps, the nucleophile attacks an electron deficient carbon with a double bond, breaking the π bond in a nucleophilic addition reaction.

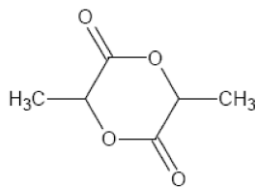
118. **C**
The RCOCH_2^- is a nucleophile and attacked the electron deficient carbon on the carbonyl in a nucleophilic addition.

119.

B

First step $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$ is the nucleophilic addition of CN^- to CH_3CHO to form $\text{CH}_3\text{CH}(\text{OH})\text{CN}$

Second step $\text{CH}_3\text{CH}(\text{OH})\text{CN} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH}$ is acidic hydrolysis



Third step $\text{CH}_3\text{CH}(\text{OH})\text{COOH} \rightarrow$ is condensation as $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ has both an alcohol and carboxylic acid group.

120.

B

Functional Group	Type of reaction	Example
Phenol	Electrophilic substitution	To substitute in a halogen onto the benzene ring
Amine	NIL	
Carboxylic acid	Nucleophilic substitution	To form acyl chloride
	Reduction	Reduce to form 1° alcohol

121.

D

Stage 1: The diamide donated a proton and is a Bronsted acid. The OH^- accepted a H^+ to form H_2O . Thus this is an acid-base reaction.

Stage 2: Bromoethane undergoes nucleophilic substitution, with the negatively charged ion acting as the nucleophile.

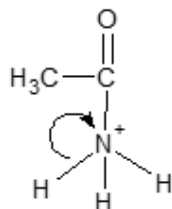
Stage 3: The amide undergoes base-catalysed hydrolysis.

122.

Answer : A (1,2,3 and 4)

1: Correct. NH_3 has a lone pair of electrons and uses it to attack the electron deficient carbon.

2: Correct. The arrow in step 3 is ~~shown~~ incorrectly. The correct arrow movement should be



3: Correct. The carbon has two electron withdrawing groups (oxygen and chlorine) bonded to it, resulting in a very electron-deficient carbon.

4: Step 2 involves the breakage of C-Cl bond. Comparing the bond energy of C-Cl (340 kJ) and C-Br (280 kJ), less energy required to break the C-Br bond, activation energy for the reaction involving ethanoyl bromide will be lower, hence the rate of reaction will be faster.

123.

Answer: B

A new bond is formed between a benzene and N of the diazonium salt. C of benzene is electron rich due to loosely held pi electron hence reacts with an electrophile.

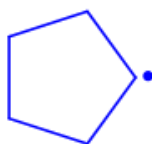
Substitution has taken place as a C-H bond of benzene is replaced with C-N bond, Hence electrophilic substitution occurs on the benzene ring.

124.

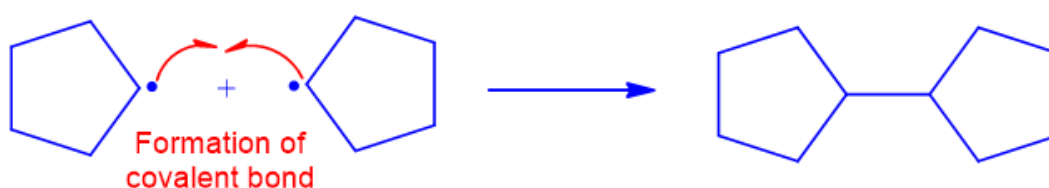
Answer: D

In **A**, **B** and **C**, the Cyclopentane units are sharing carbon atoms, whereas in **D**, the carbon atoms of each Cyclopentane unit are separate from other Cyclopentane units. In free radical substitution, the termination step between two alkyl radicals gives rise to a new C-C bond, and the number of carbon atoms in the product should be the sum of that in the alkyl radicals.

The radical formed should be



Hence the termination step between two alkyl radicals should be:

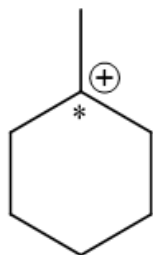


125.

Answer: D

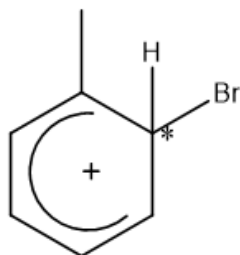
Option A: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S_N2) mechanism as it is a primary RX. There is no intermediate. The product is formed via a pentavalent transition state (C atom with * will not be sp^3 hybridised anymore because it is bonded to 5 groups).

Option B: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S_N1) mechanism as it is a tertiary RX. Intermediate is a carbocation where the C atom with * is sp^2 hybridised.



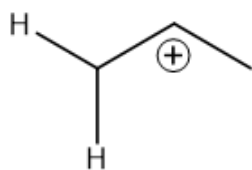
Intermediate:

Option C: C atom with * is sp^2 hybridised in the reactant. Electrophilic substitution mechanism. The C atom with * in the intermediate is sp^3 hybridised.



Intermediate:

Option D: C atom with * is sp^2 hybridised in the reactant. Electrophilic addition mechanism. The C atom with * in the intermediate is also sp^2 hybridised.

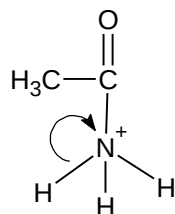


Intermediate:

126. **A**

1: Correct. NH_3 has a lone pair of electrons and uses it to attack the electron deficient carbon.

2: Correct. The arrow in step 3 is shown incorrectly. The correct arrow movement should be



3: Correct.

127. **D**

Option 1 is wrong.

C–F bond is very strong and will not be broken by sunlight.

Option 2 is wrong.

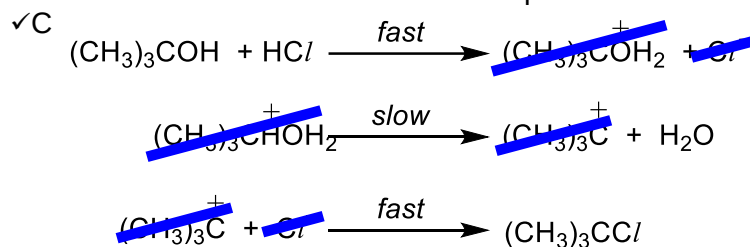
$\text{H}\bullet$ radicals are not formed during propagation. Hence H_2 gas cannot be produced.

Option 3 is correct.

128. **B**

✓A $(\text{CH}_3)_3\text{COH}$ acts as a base to accept H^+ to form the conjugate acid $(\text{CH}_3)_3\text{CO}^+\text{H}_2$

✗B HCl acts as an acid to protonate the $-\text{OH}$ group in $(\text{CH}_3)_3\text{COH}$ to make it a better leaving group so as to form the carbocation in step 2.



✓D Steps 2 and 3 are representative of the $\text{S}_{\text{N}}1$ mechanism.

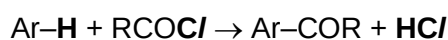
129. **A**

A✗ The alkyl group is a ring-activating group. Hence alkylbenzene will react faster than benzene.

B✓ Anhydrous AlX_3 and FeX_3 can be used in Friedel-Crafts alkylation to generate the carbocation.

C✓ Due to the bulky alkyl group, the 2-position is sterically hindered and hence the $\text{CH}_3\text{CO}-$ group will preferentially go to the 4-position.

D✓ It is an electrophilic substitution:



130. **D**

A: Butan-2-ol acts as a Brønsted base and accepts a H^+ from H_2SO_4 .

B: H_2SO_4 is reacted in step 1 and regenerated at the end of step 3, acting as a catalyst.

C: HSO_4^- can act as a nucleophile and be attracted to the carbocation $\text{CH}_3\text{C}^+\text{CH}_2\text{CH}_3$ to form the side product.

D: Tertiary carbocations are more stable than primary carbocations due to the presence of more electron-donating alkyl groups to disperse the positive charge on C^+ , hence tertiary alcohols are more likely to react via this mechanism.

Hydrolysis

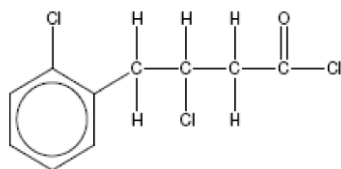
131. **D**

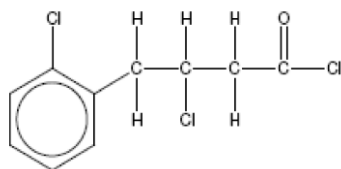
Reactivity is related for bond strength. The 3 factors that affect bond strength in priority are

- 1) Bond order
- 2) Bond length
- 3) Bond polarity

Hence, option C and A are eliminated first.

The stability of the halide ion does not relate to the strength of the C-F bond.

132. **C**

2 moles of  gives of 4 moles of Cl^- from the acyl chloride functional group and the alkyl chloride functional group that undergoes nucleophilic substitution by the OH^- .

2 moles of Ag are Cl^- formed.

$$M_r \text{ of AgCl/precipitate} = (107.9 + 35.5) \times 4 = 573.6$$

133. **B**

T undergoes hydrolysis least readily due to the C—Cl bond having partial double bond character for the sideways overlap of the p orbitals from the alkene group to the p orbitals of the Cl. Furthermore, the electron rich C atom in $\text{C}=\text{C}$ also repel the incoming nucleophile.

R undergoes hydrolysis most readily due to the C atom in acyl chloride being highly electron deficient as it is attached to electron withdrawing O and Cl.

The C—Cl bond in **S** is stronger than the C—Br bond in **U** and hence **U** undergoes hydrolysis more readily than **S**.

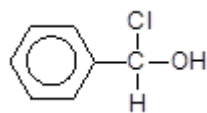
134. **C**

W does not give any precipitate over time, which would most likely mean that the C—Br bond cannot be broken and is most likely to be $\text{C}_6\text{H}_5\text{Br}$ where the C—Br bond has partial double bond character. Furthermore, the electron rich C atom in benzene also repel the incoming nucleophile.

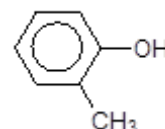
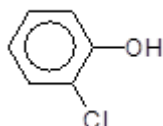
Z gives the most precipitate over time which means the C – Br bond is most easily broken. It undergoes hydrolysis most readily due to the C atom in acyl bromide being highly electron deficient as it is attached to electron withdrawing O and Br.

Y gives more precipitate than X over time. Based on the remaining options, BrCH₂CH₂Br will give more precipitate over time than C₆H₄(Br)CH₂Br as the Br bonded directly on the benzene will not be substituted.

135.

C

is an aliphatic alcohol and the conjugate base that is formed does not have negative charge readily dispersed, hence it is the least acidic.



is more acidic (dissociated into H⁺ more readily) than due to the presence of electron withdrawing Cl which disperses the negative charge of its carboxylate ion to a greater extent as compared to the other carboxylic acid which has an electron donating alkyl group.

136.

A

CH₃CH₂COC/ is the most acidic as it hydrolyses in water to give CH₃CH₂COOH and HCl(aq), hence it is the most acidic.

CH₃CH₂COOH is a weak acid and dissociates partially in water to give some H⁺.

CH₃CH₂CONH₂ is neutral, pH = 7

CH₃CH₂CONH₂ is a weak base and dissociates partially in water to give OH⁻, pH >7

137.

D

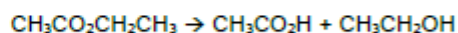
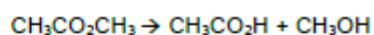
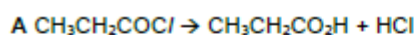
Increasing pK_b value refers to the ions being arranged from stronger base to weaker base.

A stronger base is able to donate lone pair electrons on O/N atom to accept H⁺.

For ethoxide ion, CH₃CH₂O⁻, the electron donating R- group increases the electron density on O.

For phenoxide ions and ethanoate ion, CH₃COO⁻, the lone pair electron on O is delocalised into the benzene ring and the highly electronegative C=O group respectively. The extend of delocalisation of electron is most significant in CH₃COO⁻, hence it is least ready to accept H⁺.

4-nitrophenoxide is a weaker base than phenoxide as the additional –NO₂ group is electron withdrawing, and this decreases the electron density on O, making 4-nitrophenoxide a weaker base than phenoxide.

138. **C**139. **D**

Compound **M** will be hydrolysed in water to produce compound **K** and HCl(aq) . Since HCl is a strong acid, it will provide the solution with the lowest pH (most acidic).

Compound **K**, **L** and **N** are all monoprotic weak acids. Due to the presence of electronegative Cl and Br atoms on carbon adjacent to the $-\text{COOH}$ group, compound **L** and **N** would have a more stable conjugate base as compared to compound **K** and hence more readily undergo dissociation to produce H^+ . Compound **K** would hence have the highest pH.

Since Cl is more electronegative than Br, conjugate base of compound **L** would be more stable than compound **N**. Compound **L** would thus have a lower pH (more acidic) than compound **N**.

140. **A**

The strength of basicity of a nitrogen compound depends on the availability of lone pair electron for donation with H^+ .

In both $\text{C}_6\text{H}_5\text{NH}_2$ and CH_3CONH_2 , the lone pair on N is delocalised into the benzene ring and C=O respectively. Hence, the lone pair is less available for donation as compared to $(\text{CH}_3)_2\text{NH}$. Hence, $(\text{CH}_3)_2\text{NH}$ is the most basic among the 3 species.

The highly electronegative O in the adjacent C=O group of CH_3CONH_2 is more capable of withdrawing electron from N than the C in the adjacent benzene ring of $\text{C}_6\text{H}_5\text{NH}_2$. Hence, the lone pair on N of CH_3CONH_2 is less available for donation, and is thus less basic than $\text{C}_6\text{H}_5\text{NH}_2$.

141. **D**

The strength of basicity of a nitrogen compound depends on the availability of lone pair electron for donation with H^+ . Also, the lower the pK_b , the higher the basicity.

As the lone pair is delocalised into the benzene ring, the lone pair on the N of compound **I** and **II** are less available for donation as compared to compound **III** and **IV**. Compound **I** and **II** will have a higher pK_b compared to compound **III** and **IV**.

Compound **II** with an electron withdrawing $-\text{NO}_2$ group will further draw electrons away from the N as compared to compound **I**. Hence, compound **II** will have a lower basicity than compound **I**.

Compound **III** has 2 electron donating alkyl group attached to the N which compound **IV** only has 1. Hence, compound **III** has a higher basicity (lower pK_b) than compound **IV**.

142. **Answer: C**

$\text{CF}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CO}_2\text{H}$ are both acids, both $\text{pH} < 7$, $\text{CF}_3\text{CO}_2\text{H}$ has 3 electron-withdrawing fluorine, which stabilises the conjugate to greater extent, $\text{CF}_3\text{CO}_2\text{H}$ is the strongest acid, hence lowest pH.

HOCH_2CHO has alcohol and aldehyde hence it is neutral, $\text{pH} = 7$.

$\text{CH}_3\text{CO}_2\text{Na}$ is a strong conjugate base of weak acid $\text{CH}_3\text{CO}_2\text{H}$, it undergoes alkaline hydrolysis producing OH^- , hence it has a $\text{pH} > 7$.

143. **Answer: C**

Phenol and carboxylic acid will dissociate in water to form O^- and COO^- respectively.



The D^+ can bond with the phenoxide ions and carboxylate ion. Since there are 2 phenols and 1 carboxylic acid in compound **X**, 3 hydrogen atoms could be replaced.

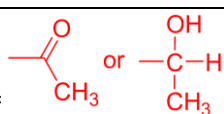
$-\text{CH}_2\text{OH}$ is an alcohol, pH neutral therefore H of OH group cannot be replaced with D.

144. **D**

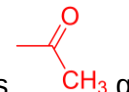
The amide functional groups will undergo alkaline hydrolysis to form amine and carboxylate ion. Phenol will undergo acid-base reaction to form phenoxide while alcohol is too weak of an acid and will not react with NaOH.

Distinguishing Test

145.

A
 Due to a lack of structure, both species will not react with alkaline aqueous iodine. Sodium metal and Tollen's reagent ($[\text{Ag}(\text{NH}_3)_2]^+$) will react with both species. Hence, both reagents will not be able distinguish between the 2 species.
However, compound P has an aliphatic aldehyde group but compound Q is a benzaldehyde derivatives. Hence, Fehling's solution (alkaline copper(II) complex) is the only reagent that can distinguish between the two.

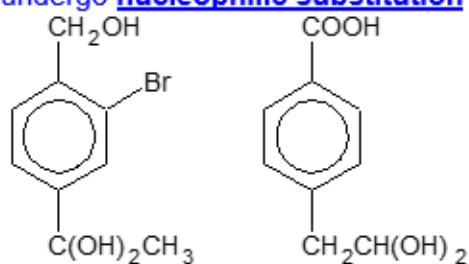
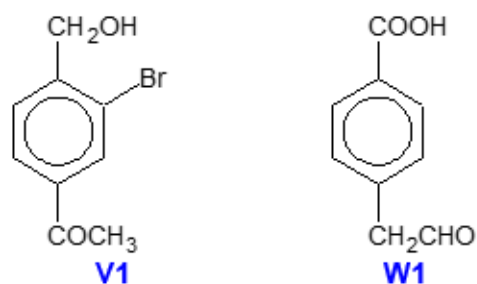
146.

C
 Compound X has group that will react with alkaline aqueous iodine. It also has an 2° alcohol group which can react with both PCl_5 (giving a white fume) and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (colour of solution change from orange to green). However, compound Y does not have any alcohol group and contain an ester instead of a methyl ketone. Upon heating with acidified potassium dichromate, compound Y undergoes acidic hydrolysis to give a 3° alcohol, which cannot be oxidised. Hence, these 3 reagents will be able distinguish between the 2 species.
Compound X contains a benzaldehyde that does not react with Cu^{2+} in alkaline solution. Aldehyde functional group is absent in compound Y and so will not react as well. Hence, Cu^{2+} in alkaline solution can not be used to distinguish between the two.

147.

D
Both compounds contain phenol group and will react with neutral FeCl_3 . Eugenol contains alkene that can react with $\text{HBr}(\text{g})$, however there is no significant observation. Since there is no aldehyde group in any of these molecules, both will not react with Fehling's reagent. Hence, there 3 reagents are not suitable for use to distinguishing between the 2 molecules.
Ginerol contains a ketone functional group but eugenol contains no carbonyl group. Hence, Eugenol will not give any orange precipitate when reacting with 2,4-DNPH but Ginerol would.

148.

Answer : D (2, 3 and 5 only)The Halogenoalkanes will undergo **nucleophilic substitution** to give alcohols.**Diols on the same C atom are unstable, hence they decompose (with the loss of water) to give the respective carbonyl compounds.**

- | | | |
|---|------------|------------|
| 1 | +ve for V1 | +ve for W1 |
| 2 | -ve for V1 | +ve for W1 |
| 3 | -ve for V1 | +ve for W1 |
| 4 | +ve for V1 | +ve for W1 |
| 5 | +ve for V1 | -ve for W1 |

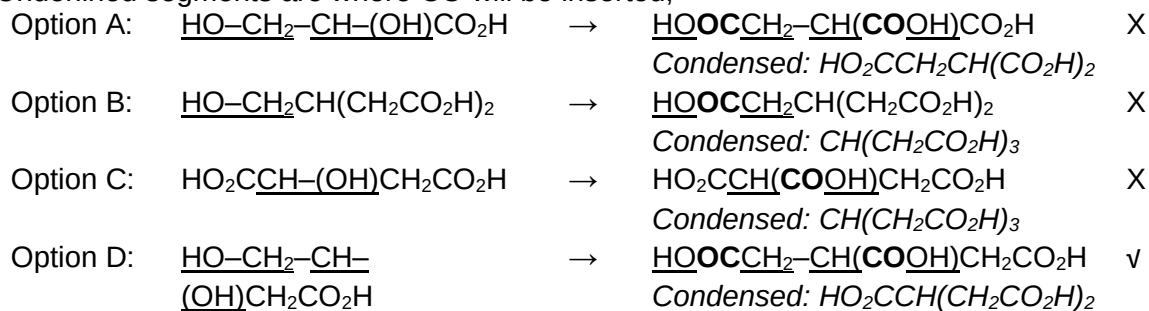
Pattern Identification

149.

D

In the example provided, the **CO** is inserted between the $\text{CH}_3\text{--OH}$ bond to give CH_3COOH . Likewise, to identify the starting compound which results in $\text{HO}_2\text{CCH}(\text{CH}_2\text{CO}_2\text{H})_2$ via the same method, we need to first identify the --OH group in each option and insert a **CO** group between the RC--OH bond, converting it into --COOH .

Underlined segments are where **CO** will be inserted,



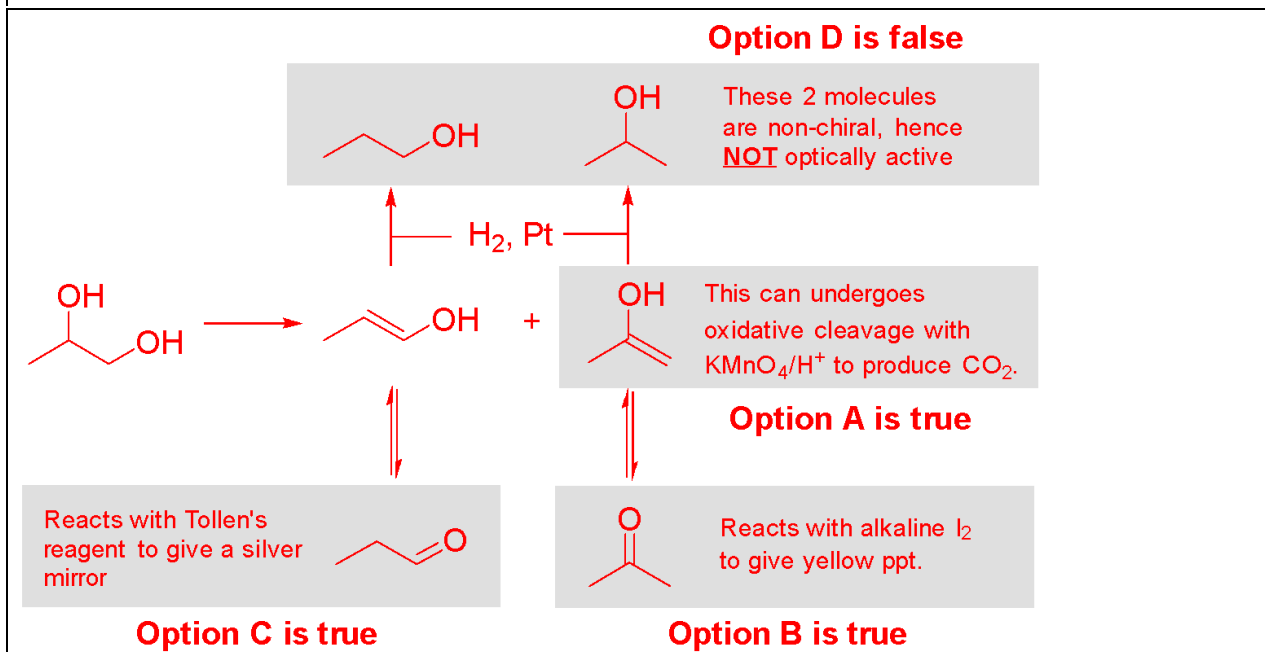
150.

A

Nucleophiles are electron rich sources and will react with electron deficient sites.

Since the carbon atom of the isocyanate group is bonded to 2 highly electronegative N and O atoms, this carbon atom is the most electron deficient site in the whole molecule, resulting in it being the most probable site for nucleophilic attack.

151.

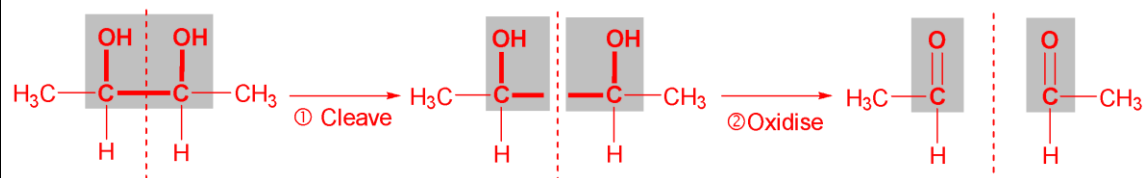
D

152.

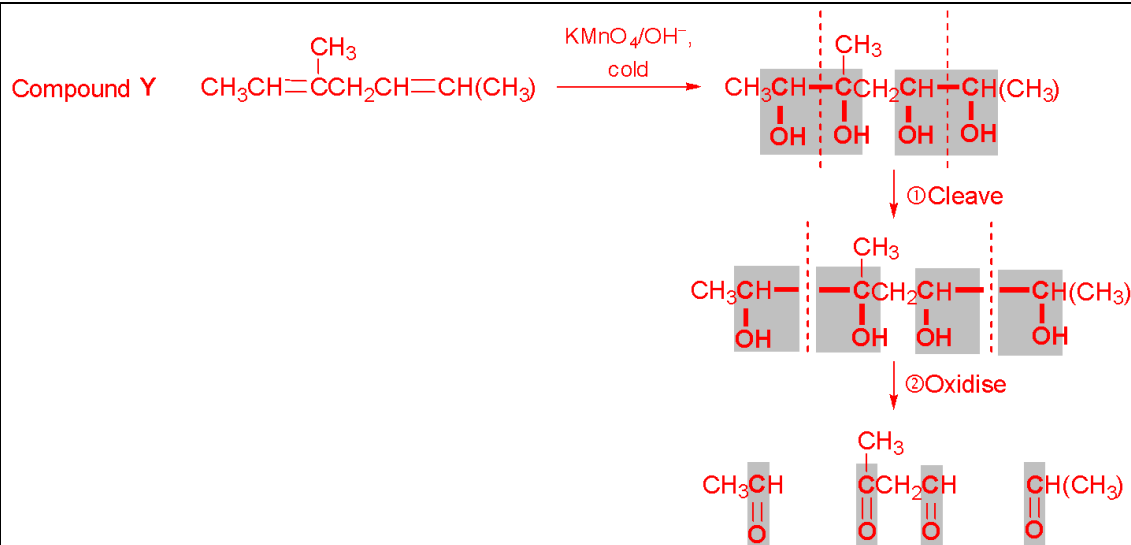
A

In the example that was given, the IO_4^- 1) cleaves the diol at the C–C bond where the 2 – OH groups are situated. It then 2) oxidises the –C–OH group into –C=O group.

Pattern:



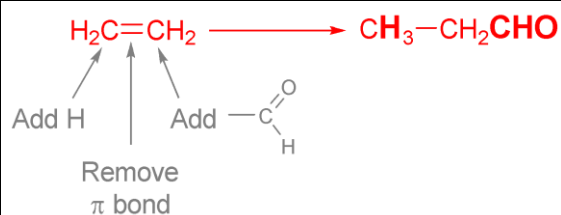
Following this pattern,



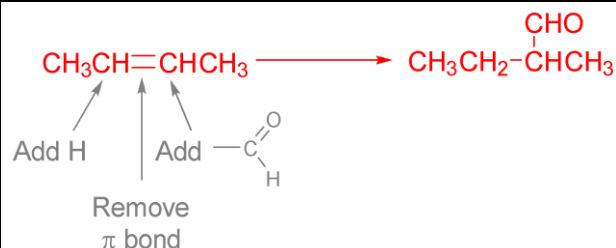
153.

A

Based on the equation given, we can observe the following pattern:



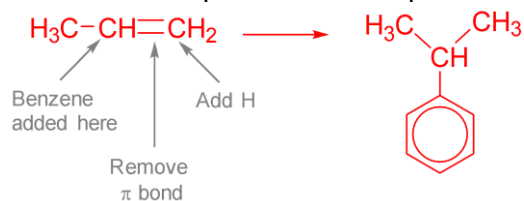
Applying the same pattern to but-2-ene,



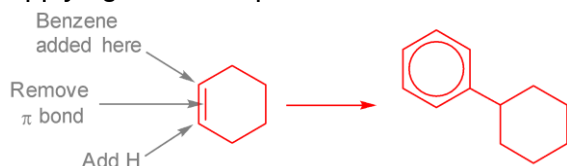
154.

A

From the example, we see the pattern to recognise is as follow:



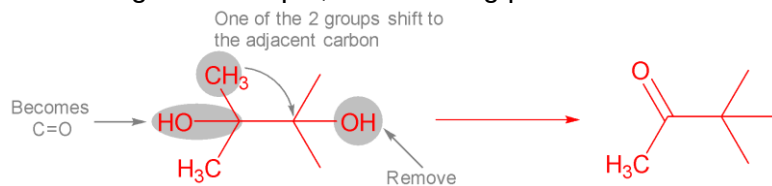
Applying the same pattern for reaction between benzene and cyclohexene,



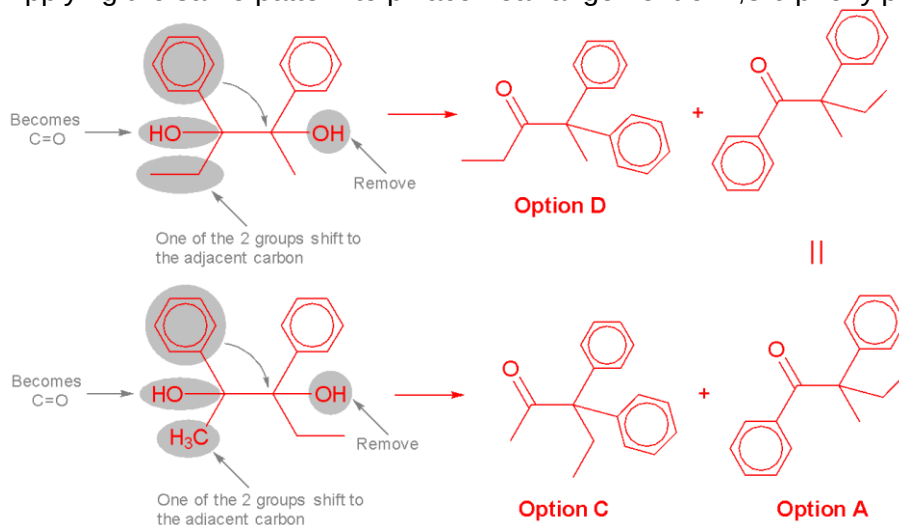
155.

B

From the given example, the following pattern can be observed,



Applying the same pattern to pinacol rearrangement of 2,3-diphenylpentane-2,3-diol,



The is no $-\text{CH}_2\text{C}_6\text{H}_5$ group present on any of the 2 carbons attached to the $-\text{OH}$ groups that can shift during the rearrangement to produce option B.

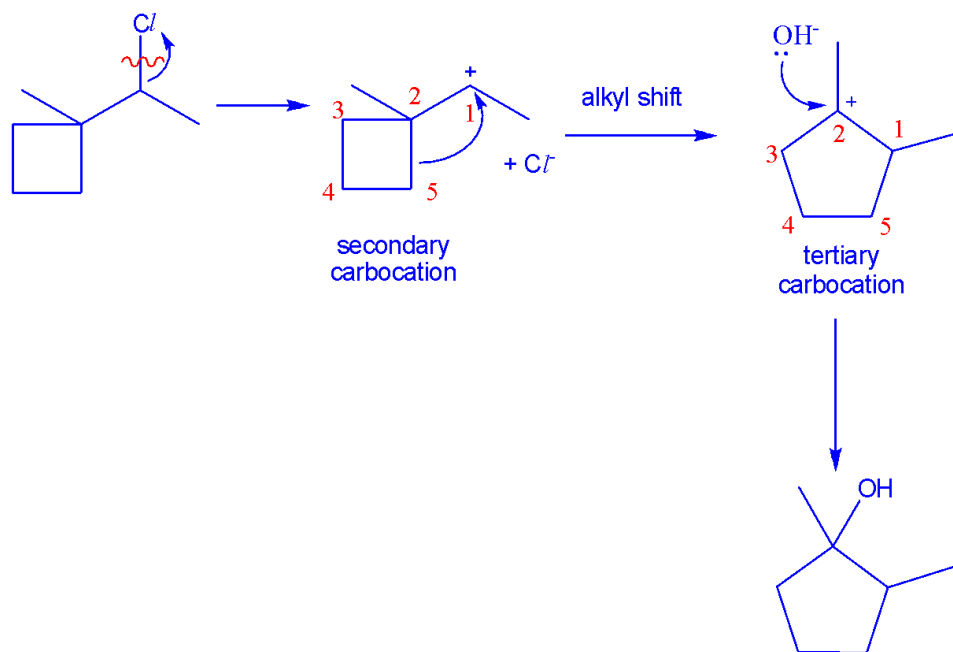
156. **C**

A is incorrect. The nucleophile used is $^-\text{COOCH}_3$.

B is incorrect. The nucleophile used is $\text{CH}_3\text{COOCH}_2^-$.

C is correct. The nucleophile used is $^-\text{CH}_2\text{COOCH}_3$ and it reacts with an aldehyde $\text{CH}_3\text{CH}_2\text{CHO}$.

D is incorrect. The nucleophile used is $^-\text{CH}_2\text{COOCH}_3$ but it reacts with a ketone CH_3COCH_3 .

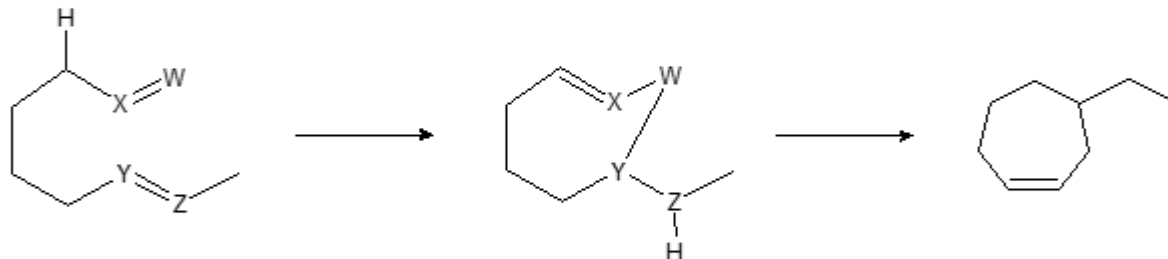
157. **B**

158.

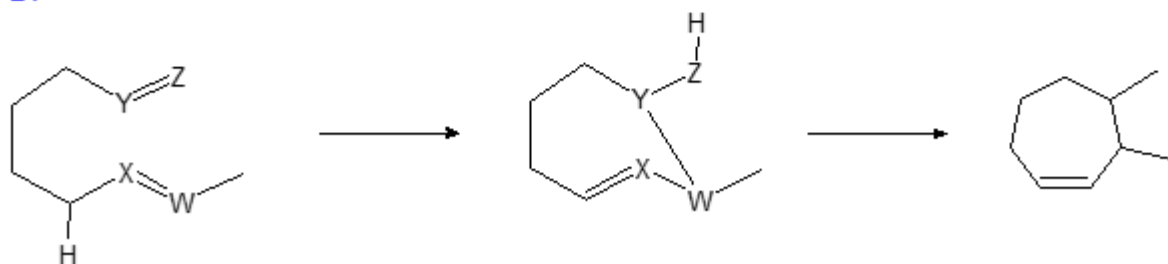
Answer: A



C:



D:

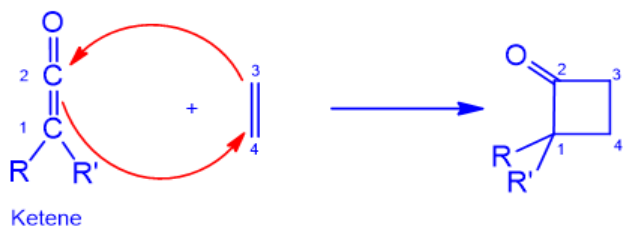


159.

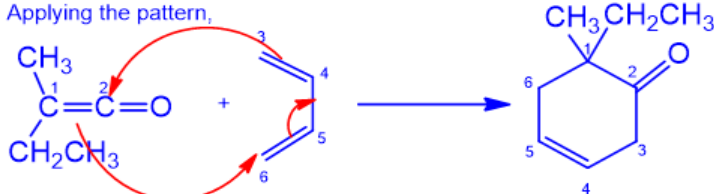
D

B cannot be the correct answer as there would be a loss of 1 C from the reactants to molecules A and B. C is not the correct answer because there is an addition of 2 H due to a missing C=C. (by comparing the M_r of the reactants and C). In the given reaction, the number of H and C and O should still stay the same after the cycloaddition reaction.

Recognising the pattern,



Applying the pattern,



160.

B

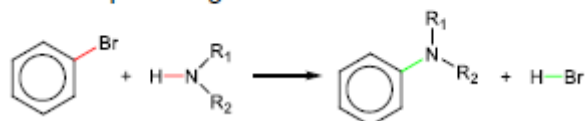
A is incorrect as the reaction does not involve the ester.

C is incorrect as it has one missing -CH_2 .

D has the double bond at the wrong position.

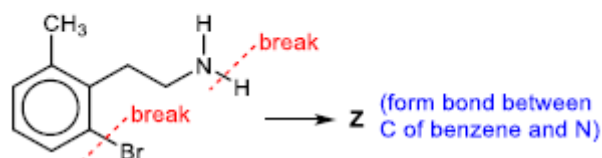
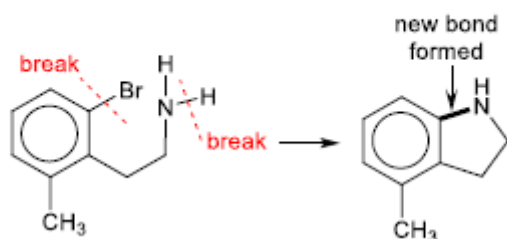
161.

This is a pattern recognition question, where the question teaches you about an unseen reaction. The way to approach such a question is to use the example given to identify what bonds have been formed and broken, and that knowledge to apply it to the question given.

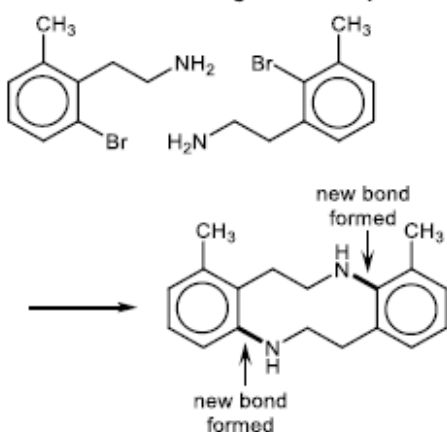
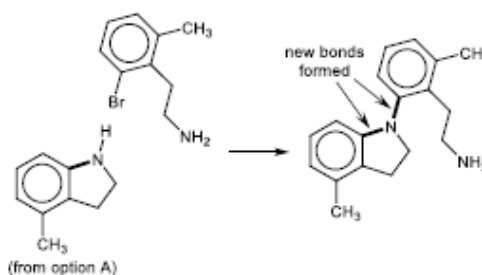
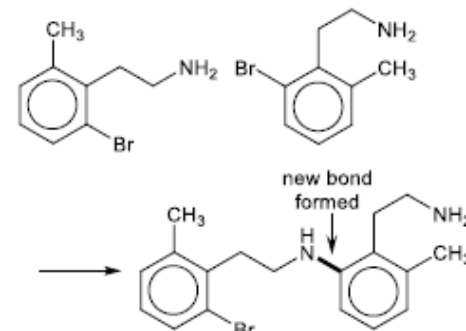


Bonds broken = C-Br and N-H
Bonds formed = C-N and H-Br

Apply this to the structure given.

**A** Possible structure for Z, intramolecular reaction**B** Not possible.

this is not the compound given in the question

**Answer: B****C** Possible structure for Z, can be formed from product in Option A with another reactant.**D** Possible structure for Z

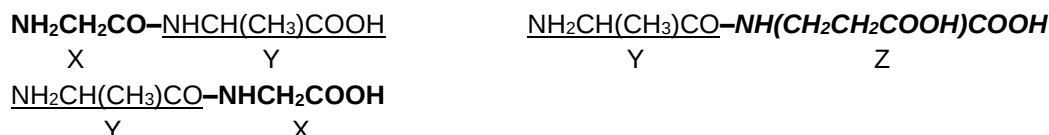
Amino Acids & Proteins

162.

B

Hydrolysis occurs only at the amide bond. Since it is a tetrapeptide, there are 3 amide bonds present in it which can be hydrolyse to give the 3 dipeptide sequences. To find the sequence of the tetrapeptide, first identify the monomers by locating where the amide bonds are.

Representing each monomer with a symbol for easier referencing,



Since monomer Z only appeared once, monomer Z is at the terminal end of the tetrapeptide. Only Option B and D could be the answer.

Again, locating the amide bonds and identifying the monomer sequence,

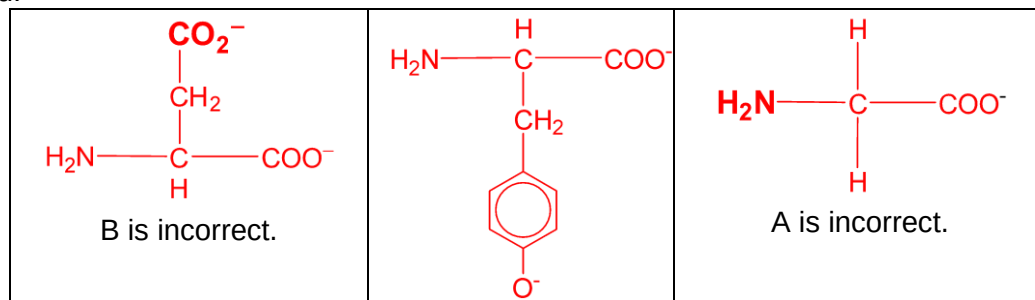
		Dipeptide Sequence
A	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}-\text{NHCH}(\text{CH}_2\text{CH}_2\text{COOH})\text{CO}-\text{NHCH}_2\text{CO}-\text{NHCH}(\text{CH}_3)\text{COOH}$	YZ, ZX, XY
	Y Z X Y	
B	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}-\text{NHCH}_2\text{CO}-\text{NHCH}(\text{CH}_3)\text{CO}-\text{NHCH}(\text{CH}_2\text{CH}_2\text{COOH})\text{COOH}$	YX, XY, YZ
	Y X Y Z	
C	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}-\text{NHCH}(\text{CH}_2\text{CH}_2\text{COOH})\text{CO}-\text{NHCH}(\text{CH}_3)\text{CO}-\text{NHCH}_2\text{COOH}$	YZ, ZY, YX
	Y Z Y X	
D	$\text{NH}_2\text{CH}_2\text{CO}-\text{NHCH}(\text{CH}_3)\text{CO}-\text{NHCH}(\text{CH}_3)\text{CO}-\text{NHCH}(\text{CH}_2\text{CH}_2\text{COOH})\text{COOH}$	XY, YY, YZ
	X Y Y Z	

163.

D

Alkaline hydrolysis occurs at the amide bonds.

Upon alkaline hydrolysis, and left in environment of pH 10 (in the gel) the following monomers are obtained:

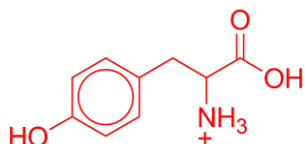
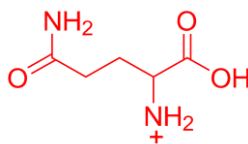
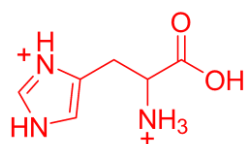
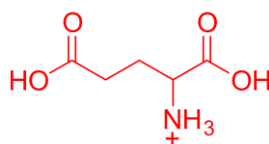


Option C is not an α -amino acid, hence it is not a product of the hydrolysis.

164.

B

At pH 4 (acidic buffer), N atoms with available lone pairs for donation to H^+ will be positively charged. Hence, the molecules in the 4 options will bear the following charges,

A**C****B****D**

Since option B (with an overall charge of +2) has the highest positive charge, it will move most readily towards the cathode.

165.

D

Side-chain $-NH_3^+$ group will not dissociate as its pK_a value (10.5) is above pH 9.5.

166.

Answer: A

Option B is incorrect: Both compounds are not able to react with ethanoic acid to give amide. Acid-base neutralization would occur, producing a salt.

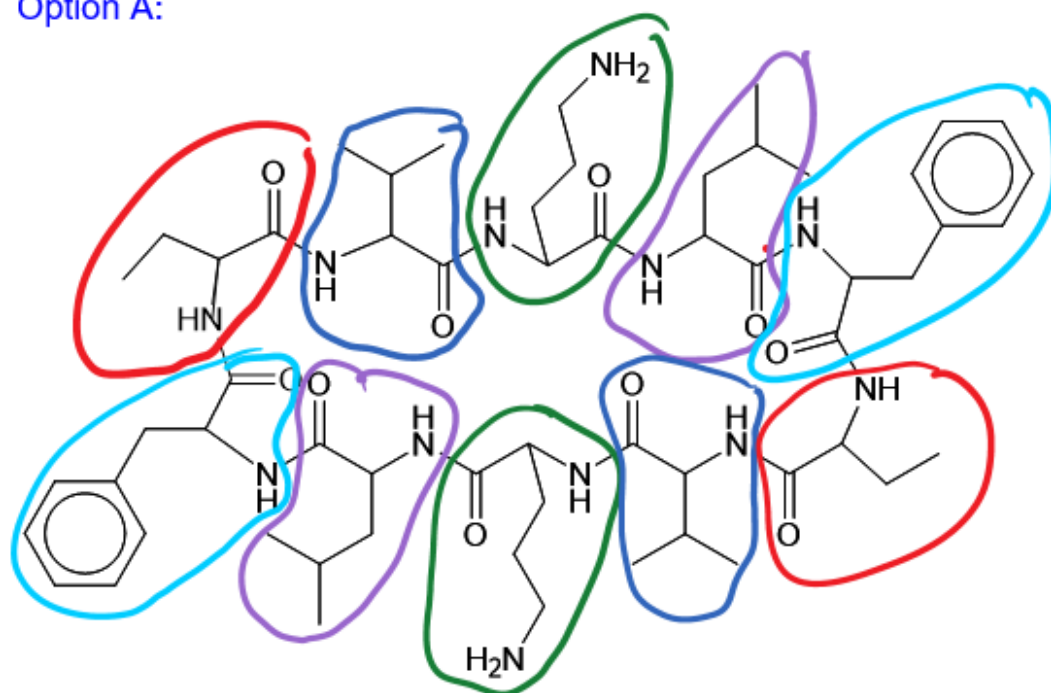
Option C is incorrect: Both compounds are not able to react with $NaBH_4$ in methanol to give alcohol. They must react with $LiAlH_4$ in dry ether.

Option D is incorrect: Both valine and 3-aminopropanoic acid are soluble in water due to formation of ion-dipole interactions, not hydrogen bonding.

167.

Answer: A

Option A:



Gramicidin Soviet

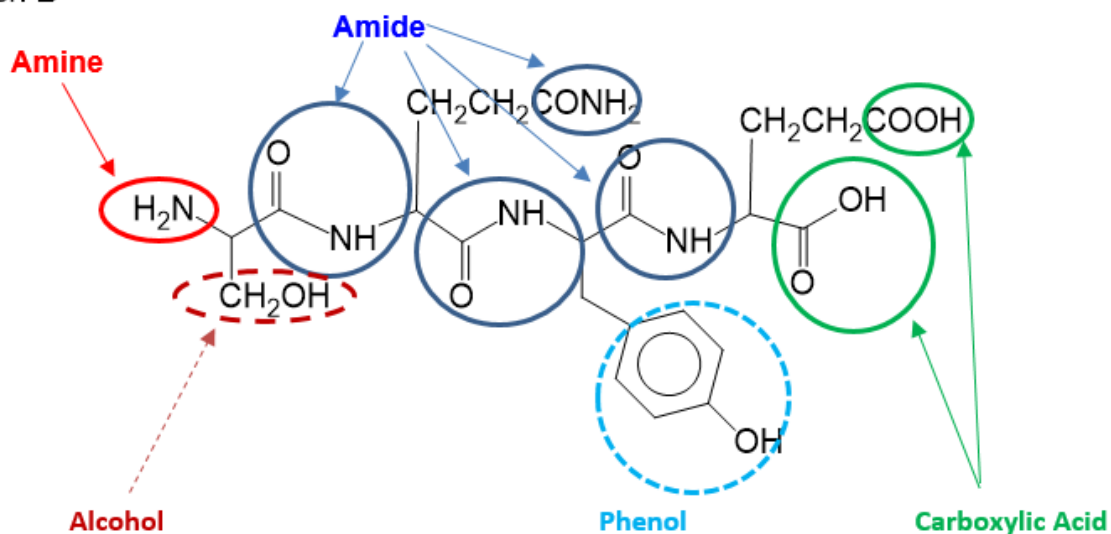
There are 5 different amino acids (marked by the different colours).

Option B: There are 10 amide bonds.

Option C: 10 moles of amide bonds will be hydrolysed by 10 moles of hot dilute H_2SO_4 . However, there are amine groups in the side-chains which would also be neutralised by dilute H_2SO_4 . Hence, more than 10 moles of hot dilute H_2SO_4 will react with 1 mole of Gramicidin Soviet.

Option D: Upon reaction with hot dilute NaOH , the products formed are ionic salts (the COOH groups obtained after hydrolysis of amide bonds will be neutralised to form COO^-). These salts have high melting point as they can form strong electrostatic forces of attraction between ions, and NOT form intermolecular hydrogen bonding.

168.

Answer: **B**

Hence, 1 mol of **J** will react with 7 mol of NaOH (aq) (Basic hydrolysis of **amides**, neutralisation of **carboxylic acid** and **phenols**).

1 mol of **J** will react with 5 mol of HCl (aq) (Acidic hydrolysis of **amides**, neutralisation of **amine**).

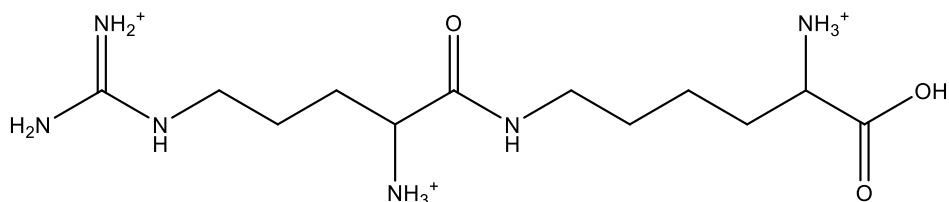
When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react (**alcohol**, **phenol** and **amine**).

When 1 mol of **J** reacts with Na(s) , 2 mol of hydrogen gas will be given out. (**Phenol**, **alcohol** and **carboxylic acid**).

169.

B

- A** Incorrect – amine groups in **U** undergo nucleophilic substitution with chloroethane
- B** Correct – amide group (peptide linkage) hydrolysed to give two amino acids.
- C** Incorrect – only 3 amino groups react with hydrochloric acid and get protonated as shown below; the amide group (neutral) does not react with hydrochloric acid at r.t.



- D** Incorrect – At pH 3, amine groups are protonated and **U** is likely to have a net positive charge and so, is likely to be found near the cathode.

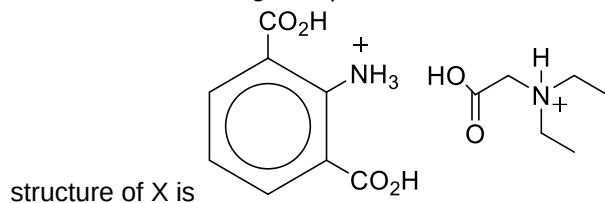
170.

D

A is incorrect: Amide undergoes reduction with LiAlH_4 to give amine. The O in C=O will be replaced with 2 hydrogen atoms and hence W has 2 more H atoms than lidocaine.

B is incorrect: Lidocaine undergoes base hydrolysis with NaOH(aq) to form an amine and a carboxylate salt as the products present in Y.

C is incorrect: Reagents provided will result in acidic hydrolysis to occur first, before oxidation. The



D is correct: No heating involved, therefore only an acid base reaction has occurred without hydrolysis

