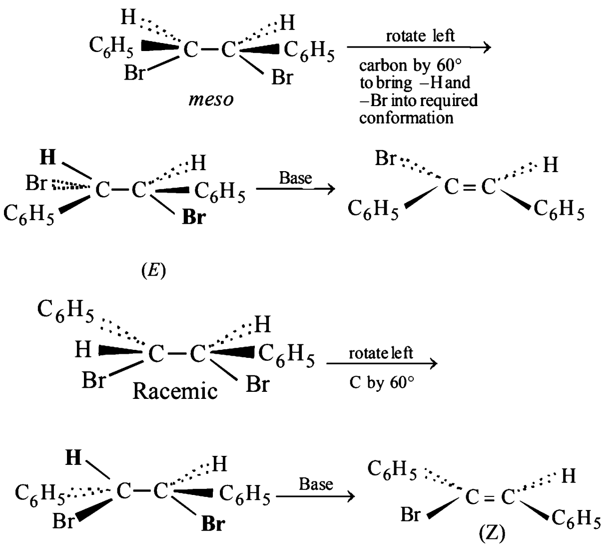
DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC10

1. **(b)** For an E2 reaction, – H and –X must be oriented anti and coplanar (at a dihedral angle of 180°) to one another



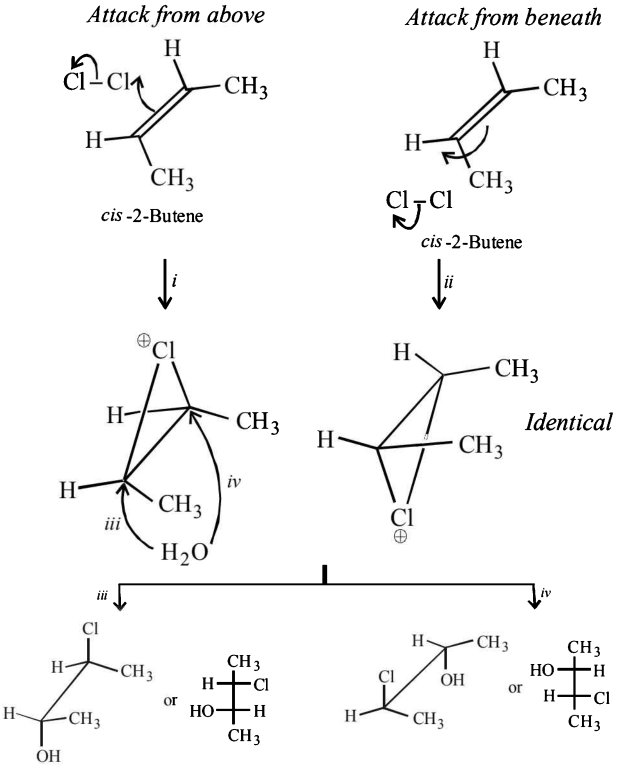
2. **(d)** The nature of hybridisation of a carbon can be ascertained by knowing the total number of electron pairs (*ep*) in the hybrid orbitals of that carbon atom : $ep = \sigma bp + lp$

σbp is the number of bond pair in hybrid orbitals involved in σ bond formation, while lp is the number of lone pair in hybrid orbital. The nature of hybridisation is thus ascertained as sp^3 (when ep is 4), sp^2 (when ep is 3) and sp (when ep is 2).

	(i) $CH_2=\overset{+}{C}H$		(ii) $CH_3\overset{-}{C}HCH_3$		(iii) $CH_2=\overset{-}{C}H$	
σbp	3	2	4	3	3	2
lp	0	0	0	1	0	1
ep	3	2	4	4	3	3
Hybrid.	sp^2	sp	sp^3	sp^3	sp^2	sp^2

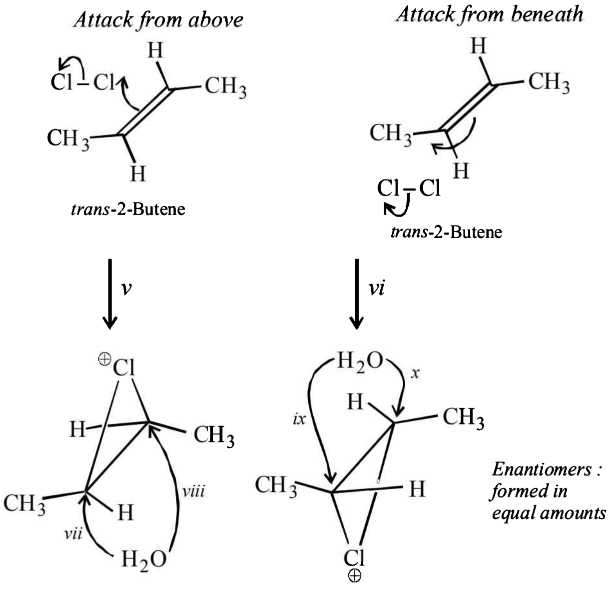
	(iv) $CH\equiv\overset{-}{C}$		(v) $CH_3\dot{C}(CH_3)_2$	
σbp	2	1	4	3
lp	0	1	0	0
ep	2	2	4	3
Hybrid.	sp	sp	sp^3	sp^2

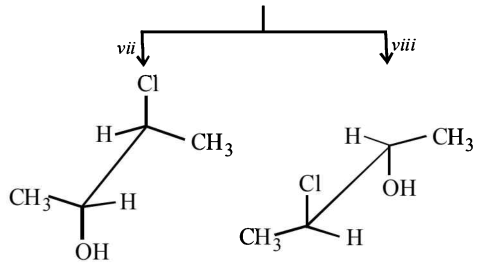
3. **(c)** Halohydrin formation is an *anti*-addition reaction in which same cyclic chloronium ion is formed in *cis*-but-2-ene whether Cl_2 attacks from the top side or from the bottom side of the molecule. Nucleophile now adds on this chloronium ion from the opposite side forming *threo* halohydrin.



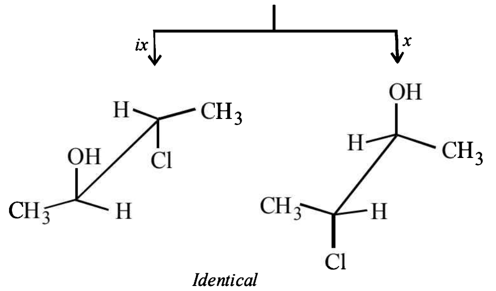
threo-3-Chloro-2-butanol (enantiomers formed in equal amounts, hence racemic modification)

However in *trans*-2-butene two different (an enantiomeric pair) cyclic chloromium ions will be formed, one due to attack from above and another due to attack from below. However, each enantiomer gives only one chlorohydrin on reaction with nucleophile (H_2O) leading to two enantiomeric chlorohydrins.



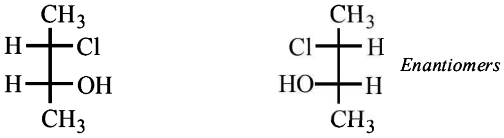


Identical



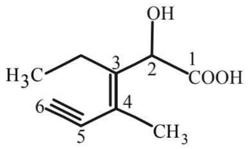
Identical

or or



erythro-3-Chloro-2-butanol
Racemic modification

4. **(a)**



IUPAC name of the structure is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid

5. **(b)** Carboxylic acids are stronger acids than $\overset{\oplus}{-NH_3}$ because the corresponding conjugate base ($-COO^-$) is more stable than $-NH_2$. Hence Y is the strongest acid. Since – COOH has – I effect which decreases with distance, therefore, effect is more pronounced in Z than in X. As a result, Z is more acidic than X. Hence the true option is Y > Z > X.

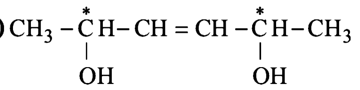
6. **(b)** Percentage of nitrogen by Kjeldahl's method

$$= \frac{14}{1000} \times \frac{\text{Normality of acid} \times \text{vol. of acid used}}{\text{wt. of organic compound}}$$

Mass of organic compound = 0.5 g
Unused acid required = 80 mL of 0.5 M NaOH
= 80 mL of 0.5 N NaOH
≡ 40 mL of 0.5 M or 1 N H_2SO_4
Acid used for absorption of ammonia
= (50 – 40) mL of 1 N H_2SO_4
= 10 mL of 1 N H_2SO_4

$$\% \text{ of nitrogen} = \frac{1.4 \times 1 \times 10}{0.5} = 28\%$$

7. **(a,d)**



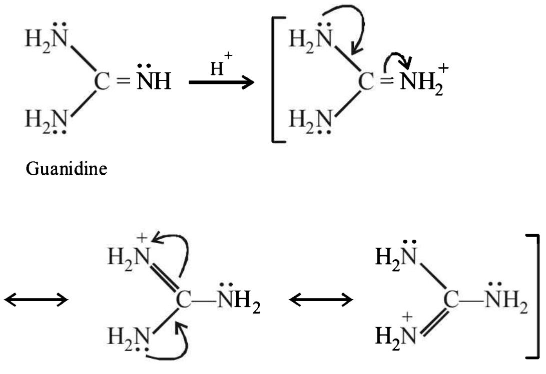
$$CH_3-\overset{*}{\underset{\mid}{C}}H-CH=CH-\overset{*}{\underset{\mid}{C}}H-CH_3$$
$$\qquad OH \qquad\qquad\quad OH$$

Stereoisomer	**Configuration**		
I	*d*	*cis*	*d*
II	*l*	*cis*	*l*
III	*d*	*cis*	*l*
IV	*d*	*trans*	*d*
V	*l*	*trans*	*l*
VI	*d*	*trans*	*l*

Enantiomers	I and II; IV and V *cis* *trans*
Diastereomers	I (or II), III (or IV), V and VI
Meso	III and IV

8. **(a,b,c)** Lone pair of electrons on N_9 belongs to *p* orbital, hence involved in delocalisation, while the lone pair of electrons on other N's lies in sp^2 orbitals; which being static are available for protonation.

9. **(a, c,d)** On the basis of hybridisation, N (sp^3) of NH_2 with *s* less character should be more basic than N (sp^2) of the imino (= NH) group. However, N of imino group is more basic and it is this nitrogen which is protanated because its conjugate acid is resonance hybrid of three equivalent structures which accounts its unusual stability.



Guanidine

Conjugate acid of guanidine

Unusual stability of the conjugate acid of guanidine explains why guanidine is the strongest organic known base

10. **(a,c)** (a) has chiral N and also resolvable because it has a resolvable mirror image.

(b) has chiral N but not resolvable because of rapid N-inversion

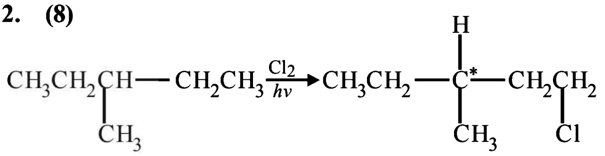
(c) has chiral N and chiral C and also resolvable because of presence of bulky alkyl groups.

(d) –COOH groups are small, hence do not provide sufficient steric hindrance to prevent rotation about C–C single bond, hence compound is non-resolvable.

11. (3) Alcohols give CAN test while phenol gives $FeCl_3$ test. So compounds containing both groups will give both coloured test. So the answer is:

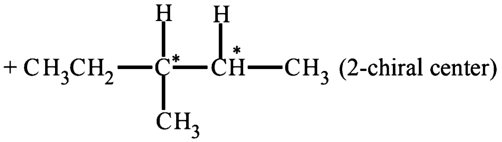
V, VI, and VII.

12. (8)



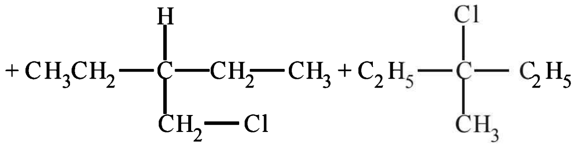
$$CH_3CH_2\underset{CH_3}{CH}-CH_2CH_3 \xrightarrow[hv]{Cl_2} CH_3CH_2-\overset{H}{\underset{CH_3}{C^*}}-CH_2\underset{Cl}{CH_2}$$

(1-chiral centre)
2-stereo-isomers
(*d* and *l*)



$$+CH_3CH_2-\overset{H}{\underset{CH_3}{C^*}}-\overset{H}{\overset{*}{C}H}-CH_3 \text{ (2-chiral center)}$$

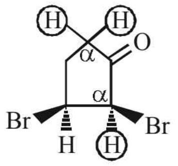
4- stereo isomers (Two pairs of enantomers)



$$+CH_3CH_2-\overset{H}{\underset{CH_2-Cl}{C}}-CH_2-CH_3+C_2H_5-\overset{Cl}{\underset{CH_3}{C}}-C_2H_5$$

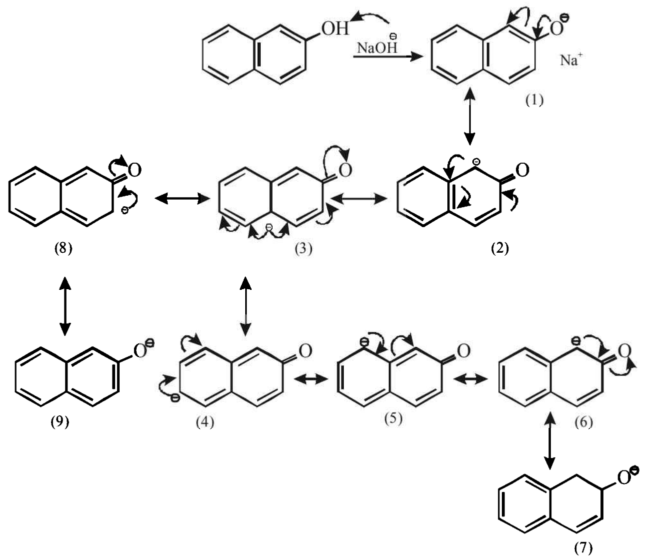
Therefore, total isomers = 8.

13. (3)



There are 3-α-H-atoms which are acidic due to EWG (>C = O) and they can be replaced by deuterium in basic medium as shown by circle.

14. (9)



15. (c) All amines have a lone pair of electrons on N which enables them to form a H bond. However, tertiary amines although can form H–bond with water or other hydroxylic solvents, it does not form H-bond with its second molecule because of absence of H on N. Only lower amines (1°, 2° as well as 3°) are quite soluble in water, solubility in water decreases with the increase in the size of the alkyl group.

16. (d) Although the mirror image of $R_1R_2R_3\ddot{N}$ type of amine is not superimposable on its object, yet the molecule is optically inactive because of rapid inversion of configuration between the two arrangements i.e. the two enantiomers are only hypothetical, these are not isolated.

17. (a) Acid weakening groups are electron donating and hence they activate the ring toward the attack by an electrophile.

18. (d) The H^- (in aldehydes) formed due to C – H cleavage and CH_3^- (in ketones, e.g. acetone) formed due to C – C cleavage are very poor leaving groups, hence can't be removed.

19. A-q, s; B-q, s; C-p, s; D-r

(A) $\underset{\text{Diazoacetic ester}}{N_2CHCOOC_2H_5} \xrightarrow{\text{heat}} \underset{\text{Carbene (neutral)}}{:CHCOOC_2H_5} + N_2$

(B) $\underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{\text{heat}} \underset{\text{Carbene (neutral)}}{:CH_2}$

(C) $CH_3N=NCH_3 \xrightarrow{\text{heat}} \underset{\text{Methyl radical (neutral)}}{{}^{\bullet}CH_3} + N_2$

(D) $C_6H_5-N^+\equiv NCl^- \longrightarrow \underset{\text{(although, unstable)}}{\underset{\text{Carbocation}}{C_6H_5^+}} + N_2$

20. A-q; B-p, q, r; C-p, q, s; D-q

(A) Here although two products are possible, only one is formed, the reaction is 100% stereoselective.

(B) The reaction involves the addition of Br_2 on *trans*-alkene to form 100% *meso* product. It is **stereospecific** in the sense that it involves the addition on a stereoisomer (*trans*) and forms a stereoisomeric product (*meso*). Further every stereospecific reaction is **stereoselective**. Since here cyclic bromonium ion is formed as an intermediate, the two bromine atoms add in *anti*-manner.

(C) This reaction is just the reverse of the above one, i.e. it involves the conversion of an optical isomer to geometrical isomer through elimination reaction, it is stereospecific, stereoselective and involves *anti* elimination.

(D) Here one of the stereoisomeric product (95%) is formed from compound having no stereoisomerism, it is **highly stereoselective**.