Answers

Bonding and hybridisation in organic compounds

1	b	2	c	3	b	4	b	5	c
6	a	7	b	8	c	9	d	10	a
11	c	12	c	13	c	14	d	15	b
16	a	17	d	18	a	19	a	20	c
21	d	22	d	23	d	24	c	25	c
26	ac	27	c	28	c	29	c	30	d
31	c	32	c	33	d	34	c	35	c
36	a	37	c	38	c	39	d	40	b
41	c	42	a	43	c	44	b	45	b
46	a	47	b	48	c	49	a	50	c
51	c	52	c	53	c	54	a	55	d
56	c	57	c	58	a	59	d	60	a
61	a	62	d	63	c	64	b	65	b
66	b	67	b						

Dipole moment, resonance and reaction intermediates

1	b	2	b	3	b	4	c	5	c
6	d	7	c	8	d	9	b	10	c
11	d	12	b	13	a	14	c	15	d
16	b	17	d	18	b	19	a	20	a
21	a	22	a	23	b	24	c	25	c
26	b	27	b	28	b	29	d	30	b
31	c	32	c	33	a	34	d	35	a
36	a	37	b	38	b	39	a	40	d
41	d	42	b	43	d	44	b	45	b
46	a	47	b	48	d	49	b		

Organic reactions and their mechanism

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

Structural and stereo isomerism

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

Critical Thinking Questions

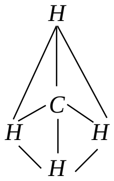
1	c	2	d	3	c	4	e	5	a
6	b	7	c	8	d	9	b	10	d
11	c	12	c	13	a	14	b	15	c
16	c	17	c	18	d	19	b	20	d
21	acd	22	c	23	b	24	c	25	b
26	a	27	a	28	c	29	a	30	d
31	c	32	b	33	b	34	b	35	c
36	bc	37	b	38	b	39	abd	40	c
41	cd	42	ac	43	c	44	c	45	b
46	c	47	b	48	d	49	d	50	a

Assertion & Reason

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

Answers and Solutions

Bonding and hybridisation in organic compounds

1. (b) 

(CH_4)

Tetrahedral

3. (b) $CH_2=CH_2$ both the carbon atoms are sp^2 hybridised.

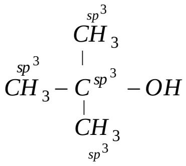
5. (c)

Type	s-character
sp^3	25%
sp^2	33.33%
sp	50%

6. (a) $\overset{sp}{CH}\equiv\overset{sp}{CH}$

7. (b) sp^2 and sp^3

$\underset{sp^3}{CH_3}-\underset{sp^2}{CH}=\underset{sp^2}{CH}-\underset{sp^3}{CH_2}-\underset{sp^3}{CH_3}$

8. (c) 

$\underset{}{\overset{sp^3}{CH_3}}-\overset{\overset{\overset{sp^3}{CH_3}}{|}}{\underset{\underset{\underset{sp^3}{CH_3}}{|}}{C}}{}^{sp^3}-OH$

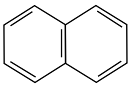
All the carbon atoms are sp^3 hybridized.

9. (d) $\underset{sp^3}{CH_3}-\overset{sp^2}{CH}=\underset{sp^2}{CH}-\overset{sp^3}{CH_2}-\underset{sp^2}{CH}=\overset{sp^2}{CH}-\underset{sp}{C}\equiv\underset{sp}{CH}$

10. (a) $\underset{sp^3}{CH_3}-\underset{sp}{C}\equiv\underset{sp}{C}-H$

11. (c) sp and sp^2

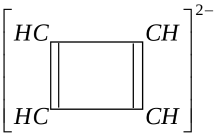
$N\equiv\underset{1}{\overset{sp}{C}}-\underset{2}{\overset{sp^2}{CH}}=\underset{3}{CH_2}$

13. (c)  π electrons = 10.

π bonds =5

hence electrons are double

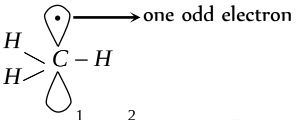
14. (d) Cyclobutadienyl anion $(C_4H_4)^{2-}$



π electrons = 8.

15. (b) $CH_3-CH_3\xrightarrow[\text{bond fission}]{\text{Homolytic}}\underset{\text{Methyl free radicals}}{\dot{CH_3}+\dot{CH_3}}$

free radical is formed which is sp^2 -hybridized.



16. (a) $Br-\underset{sp^2}{\overset{1}{CH}}=\underset{sp^2}{\overset{2}{CH}}-Br\xrightarrow[\text{Catalyst}]{H_2}Br-\underset{sp^3}{\overset{3}{CH_2}}-\underset{sp^3}{\overset{4}{CH_2}}-Br$

17. (d) (i) $\overset{sp^3}{CH_3}-\overset{sp^3}{CH_2}-\overset{sp^3}{CH_2}-\overset{sp^3}{CH_3}$

only sp^3 hybridized carbon

(ii) $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp^3}{CH_3}$

Both sp^2 and sp^3 hybridized carbon.

(iii) $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$

Only sp^2 hybridized carbon.

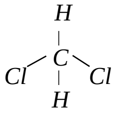
(iv) $H-\underset{sp}{C}\equiv\underset{sp}{C}-H$

Only *sp* hybridized carbon.

18. (a) (i) Benzene and its derivatives are always planar because all the carbon in benzene are sp^2 hybridized.

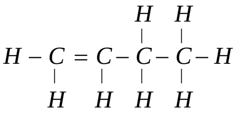
(v) $CH_2=C\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$

Both the carbon are sp^2 hybridized. Therefore planar.

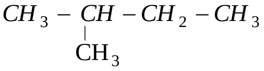
19. (a) 

Tetrahedral structure

sp^3hybridization

20. (c) 

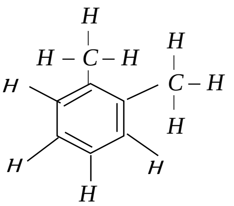
$H-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$; 11σ bonds and 1π bond.

21. (d) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

It has 3 CH_3 groups, one CH_2 group and one *CH* group.

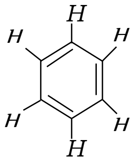
22. (d)



$O-$dimethyl benzene
or
$O-$xylene

It has 18σ bonds and 3π bonds.

23. (d)

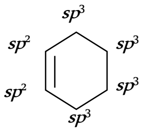


$C-C=\sigma$ bonds $=6$

$C-H=\sigma$ bonds $=\underline{6}$

12

24. (c)



Cyclo hexene

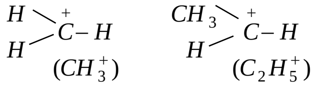
Two carbon atoms are sp^2-hybridized while remaining 4 are sp^3 hybridized.

25. (c) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{CH_2}-\overset{6}{CH_3}$

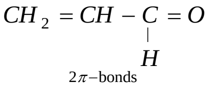
3-hexyne-1-ene

Three π bonds.

26. (a, c) Carbonium ions an *sp* hybridized species.

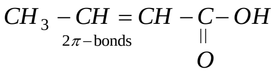


27. (c) (a) $\underset{2\pi-\text{bonds}}{H-C\equiv C-H}$ (b)



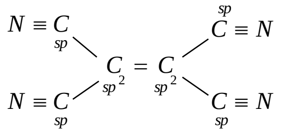
$CH_2=CH-\underset{\underset{H}{|}}{C}=O$ $2\pi-$bonds

(c) $\underset{1\pi\text{ bond}}{CH_3CH=CH_2}$ (d)



$CH_3-\underset{2\pi-\text{bonds}}{CH=CH}-\underset{\underset{O}{||}}{C}-OH$

28. (c)



29. (c) $\overset{\sigma}{H-}\overset{\sigma}{C}\underset{\pi}{\equiv}\overset{\sigma}{C}-H$ 3σ and 2π bonds are present.

30. (d) Vinyl acetylene there are 6 unhybridised orbitals.

$\underset{\underset{1}{sp^2}}{CH_2}=\underset{\underset{1}{sp^2}}{CH}-\underset{\underset{2}{sp}}{C}\equiv\underset{\underset{2}{sp}}{CH}$

(no. of unhybridised orbitals)

31. (c) Bond energy is maximum for triple bond.

32. (c) $\underset{5\sigma,\,1\pi}{CH_2=CH_2}$

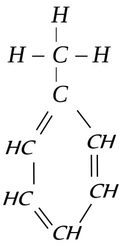
33. (d) In benzene all 6 carbons are sp^2 hybridised.

34. (c) $\underset{sp^2}{CH_2}=\underset{sp^2}{CH}-\underset{sp^2}{CH}=\underset{sp^2}{CH_2}$

36. (a) $\underset{7\sigma,\,3\pi}{CH_2=CH-C\equiv CH}$

37. (c) Propyne has one acidic hydrogen.

39. (d)



15σ and 3π.

40. (b) In CCl_4 all bond angles are same *i.e.* of $109^\circ 28'$ the carbon is *sp* hybridised.

41. (c) Geometry in sp^2-hybridisation is trigonal.

42. (a) $\underset{sp^2}{CH}=\underset{sp}{C}=\underset{sp^2}{CH}-\underset{sp^3}{CH_3}$

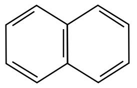
43. (c) Single bond has longest distance of bonds so C_2H_6 ethane is correct answer.

47. (b) $HC\equiv\underset{sp}{C}-\underset{sp^2}{CH}=CH_2$

48. (c) In ethylene molecule carbons are *sp* hybridised so its structure is trigonal planar

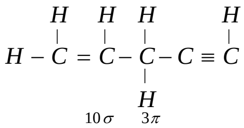
49. (a) $\underset{sp}{CH}\equiv\underset{sp}{CH}$

52. (c)



5 π bonds are present in naphthalene.

54. (a)

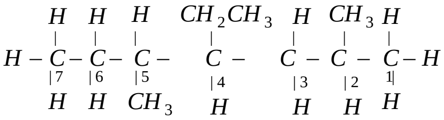


$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-C\equiv\overset{H}{\overset{|}{C}}$

10σ 3π

57. (c) $\overset{1}{\underset{sp^2}{CH_2}}=\overset{2}{\underset{sp}{C}}=CH_2$

59. (d)



$H-\underset{\underset{H}{|7}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{H}{|6}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{CH_3}{|5}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{H}{|4}}{\overset{CH_2CH_3}{\overset{|}{C}}}-\underset{\underset{H}{|3}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{H}{|2}}{\overset{CH_3}{\overset{|}{C}}}-\underset{\underset{H}{1|}}{\overset{H}{\overset{|}{C}}}-H$

2, 5 d; methyl 4-ethylheptane (5 Methyl group)

60. (a) $\overset{sp^3}{CH_3}-\overset{sp^2}{CO}-\overset{sp^3}{CH_3}$ Acetone $\overset{sp^3}{CH_3}\,\overset{sp^2}{COOH}$ Aceticacid

$\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N$ Acetonitrile $\overset{sp^3}{CH_3}-\overset{sp^2}{CONH_2}$ Acetamide

61. (a) $\overset{\downarrow 2\sigma}{CH_2}\underset{\pi}{\overset{\sigma}{=}}\overset{\downarrow\sigma}{CH}\underset{\sigma}{-}\overset{\downarrow 2\sigma}{CH_2}\underset{\sigma}{-}C\overset{\pi}{\underset{\pi}{\overset{\sigma}{\equiv}}}N$

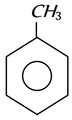
Allylcyanide

Total 9σ bond and 3π bond.

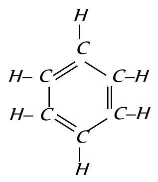
62. (d) Because hydrogen is attached with high electronegative element.

63. (c) $CH\equiv CH$

Ethyne

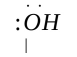


64. (b) has 15σ bonds.

65. (b) 

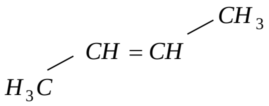
12π and 3π bonds

66. (b) The s-character of $C-H$ bond of acetylene is higher in comparison to $C-H$ bond of ethene and ethane. The electrons of the $C-H$ bond in acetylene are strongly held by carbon nuclei. This facilitates the removal of hydrogen as proton.

67. (b) 

$$\underset{9\sigma 1\pi \& 2\text{L.p}}{CH_3-\overset{\overset{\cdot\cdot}{:OH}}{\overset{|}{C}}=CH_2}$$

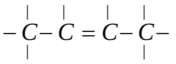
Dipole moment, resonance and reaction intermediates

1. (b) 

$\mu = 0$ symmetrical structure.

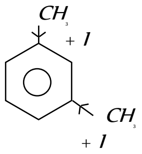
2. (b) Due to presence of two chlorine atom on the same side of carbon atom produces dipole moment in molecule.

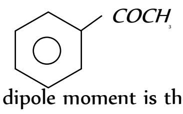
4. (c) We know that there is more difference in the electronegativities of hydrogen and chlorine. Therefore *HCl* is a polar compound.

5. (c) (i) 

$$-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{|}{C}}-$$

Trans-2 butene (u=0)

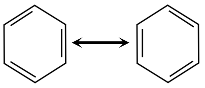
(ii) 

(iii) 

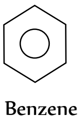
(iv) $\underset{+I}{C_2H_5OH}$

The dipole moment is the highest for Acetophenone.

6. (d) Resonance structure of molecule does not have identical bonding.

7. (c) 

All the bonds $(C-C)$ are equal in benzene. The $C-C$ bond length is 1.39Å which is in between $C-C$ bond (1.54Å) and $C=C$ (1.34Å).

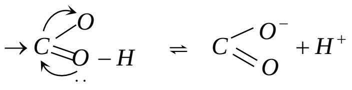
9. (b) 

(1) Molecule is planar.

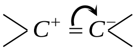
(2) 6π electrons are present.

11. (d) Benzene is unreactive instead of having 3π bonds because of resonance π -electrons are delocalized.

12. (b) Carboxylic acids are easily ionized because there is resonance in carboxylate ion due to π- electron shifting so H^+ get ionised very easily.



13. (a) Due to delocalisation of π electrons benzene has resonance.

19. (a) 

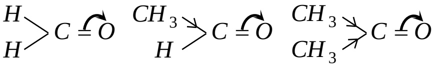
21. (a) It is hyperconjugation process.

22. (a) Triphenyl methyl cation has three benzene resonating ring so it is most stable compound.

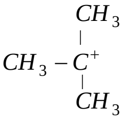
23. (b) Due to mesomeric effect (+) of – *OH* group the electron density on benzene ring increase. So the electrophile easily attacked on these electron rich center.

24. (c) Carbonyl carbon become more reactive toward nucleophilic addition by increasing the +*I* effect of alkyl group so the reactivity order is as

$$\underset{\text{I}}{HCHO} > \underset{\text{II}}{CH_3CHO} > \underset{\text{IIII}}{CH_3COCH_3}$$

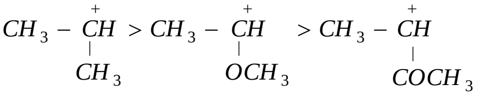


25. (c) The octet of all atoms are complete in structures (a) and (b). In structure (d) electron deficiency of positively charged carbon is duly compensated by lone pair electrons of adjacent oxygen atom while such neighbour group support is not available in structure (c).

26. (b) 

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}}$$

Due to (+*I*) effect of three methyl group 3° carbocation is more stable.

27. (b) 

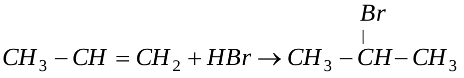
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}H} > CH_3-\underset{\underset{OCH_3}{|}}{\overset{+}{C}H} > CH_3-\underset{\underset{COCH_3}{|}}{\overset{+}{C}H}$$

28. (b) $\underset{\text{Benzyl carbanion}}{C_6H_5-CH_2^{\overline{\cdot\cdot}}} > \underset{\text{Ethyl carbanion}}{CH_3CH_2^{\overline{\cdot\cdot}}}$

$\underset{\text{Isopropyl carbanion}}{(CH_3)_2CH^{\overline{\cdot\cdot}}} > \underset{\text{Tert-butyl Carbanion}}{(CH_3)_3C^{\overline{\cdot\cdot}}}$

30. (b) 3° alcohol on dehydrogenation gives most stable carbonium ion.

32. (c) Without intermediate reaction take place as under



$$CH_3-CH=CH_2+HBr \to CH_3-\overset{\overset{Br}{|}}{CH}-CH_3$$

(According to markownikoff rule)

But the halogen bonded with terminal carbon so it take place in presence of peroxide by free radical mechanism.

$$\underset{\text{peroxide}}{R-O-OR} \to 2R\dot{O}\ ;\ HBr+R\dot{O} \to ROH+Br^{\cdot}$$

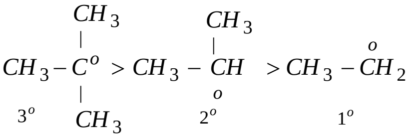
$$CH_3-CH=CH_2+Br^{\cdot} \to CH_3-C\dot{H}-CH_2-Br$$

$$CH_3-\dot{C}H-CH_2Br+HBr \to$$

$$CH_3-CH_2-CH_2Br+Br^{\cdot}$$

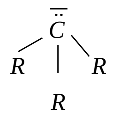
33. (a)

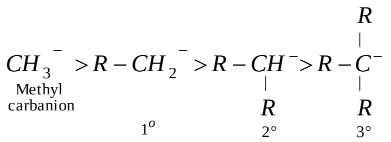
	Species	Valence electrons	Magnetic behaviour
1.	Free radical	7	Paramagnetic
2.	Carbonium ion	6	Diamagnetic
3.	Carbanion	8	Diamagnetic
4.	Carbene	6	Diamagnetic
5.	Nitrene	6	Diamagnetic

34. (d) 

$$\underset{3^o}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^o}}} > \underset{2^o}{CH_3-\underset{o}{\overset{\overset{CH_3}{|}}{CH}}} > \underset{1^o}{CH_3-\overset{o}{CH_2}}$$

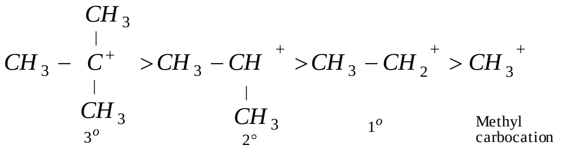
Greater the no. of alkyl groups attached to the carbon atom carrying the odd electrons, greater is the delocalization of odd electron and hence more stable is the free radical.

35. (a) 

36. (a) 

$$CH_3^- > R-CH_2^- > R-\underset{R}{CH^-} > R-\overset{R}{\underset{R}{C^-}}$$

Methyl carbanion 1^o $2°$ $3°$

37. (b) 

$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} > CH_3-\underset{CH_3}{CH^+} > CH_3-CH_2^+ > CH_3^+$$

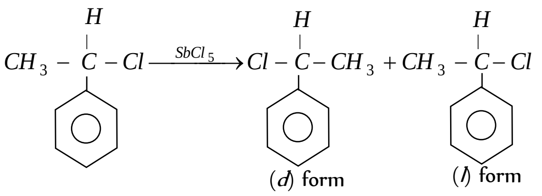
3^o $2°$ 1^o Methyl carbocation

Greater the no. of alkyl groups, greater would be the dispersal of the charge and hence more stable will be the carbonium ion.

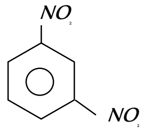
39. (a) $C-C$ bond length in benzene is 1.39Å which is in between $C-C$ $(1.54\,Å)$ and $C=C(1.34\,Å)$ because of resonance.

40. (d) $C-Cl \xrightarrow[\text{bond fission}]{\text{Heterolytic}} \underset{\text{Cation}}{C^+} + \underset{\text{Anion}}{Cl^-}$

41. (d) $CH_3CH_2OH \xrightarrow{\text{Heterolytic cleavage}} CH_3CH_2^+ + OH^-$

43. (d) 

44. (b) The reaction of an alkyl halide or aryl halide with benzene in the presence of a Lewis acid, generally $AlCl_3$ is known as Friedel Craft's reaction.

45. (b) 

gives only monosubstitution product as $-NO_2$ group is meta directing and only one m -position is possible in m -dinitrobenzene.

46. (a) According to Huckel ruel, all aromatic compounds must have $(4n+2)\pi$ electrons where n is an integer, *i.e.*, $n=0,1,2,3,...$ and possesses unusual stability due to the complete delocalisation of π -electrons.

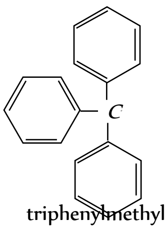
47. (b) $H-\ddot{\underset{\cdot\cdot}{O}}-H,\ :NH_3,\ R-\ddot{\underset{\cdot\cdot}{O}}-R$ - nucleophiles SO_3 has electron deficient centre (a reagent which can accept an electron pair in a reaction, is called an electrophile)

48. (d) Chlorine atom is *orth-para* directing group.

49. (b) Stability of carbonium ions.

tertiary alkyl > secondary alkyl > primary alkyl > methyl.

More the number of alkyl groups, the greater the dispersal of positive charge and therefore, more the stability of carbonium ion is observed.



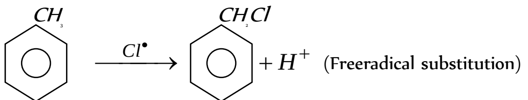
triphenylmethyl cation

Dispersal of positive charge increases with the increase in the number of benzene ring.

Organic reactions and their mechanism

1. (d) It is SN^2 type of reaction.

3. (c) $Cl_2 \xrightarrow{\text{Light}} 2Cl^\bullet$



5. (a) It is nucleophilic substitution reaction which is in first order.

9. (d) All cations are expected to act as Lewis acid since they are electron deficient in nature. However cation such as Na^+, K^+ etc. (Inert gas configuration) have a very little tendency to accept electrons. Therefore they do not acts as lewis acids in friedel Craft's reaction.

10. (d) The process of nitration takes place as below

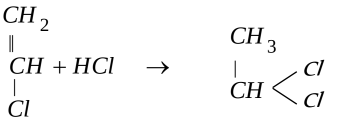
$$HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + \underset{\text{(nitronium ion)}}{NO_2^+}$$

The electrophile responsible for nitration is NO_2^+ ion.

11. (b) Dehydrohalogenation of an alkyl halide on presence of alcoholic potash is an example of elimination reaction.

$$R-CH_2CH_2-Cl + \underset{\text{alc.}}{KOH} \xrightarrow{\Delta}$$

$$RCH=CH_2 + KCl + H_2O$$

12. (d) 

$$\underset{Cl}{\overset{CH_2}{\overset{\|}{CH}}} + HCl \rightarrow \overset{CH_3}{\overset{|}{CH}} \lt^{Cl}_{Cl}$$

(1,1 dichloroethane)

It is addition reaction.

Which is according to Markownikoff rule.

13. (c) $CH\equiv CH + H_2 \rightarrow CH_2=CH_2$

That is called addition reaction.

14. (d) When methane gas is treated with chlorine in the presence of sunlight, one hydrogen of methane replaced by the chlorine atom and forms methyl chloride. The mechanism involved in this reaction is free radical mechanism. So it is an example of free radical substitution reaction.

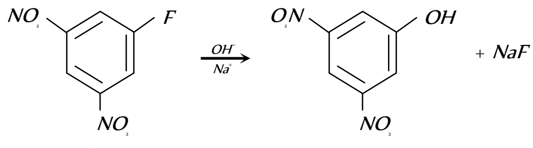
15. (c) Due to OH^- attack it is nucleophilic substitution.

16. (a) Electron deficient species (in complete octet) acts as an electrophile *i.e.* BCl_3 .

17. (a) $NO_2^{\oplus}$ is produced when conc. HNO_3 reacts with conc. H_2SO_4 .

$$HNO_3 + H_2SO_4 \rightarrow HSO_4^- + NO_2^{\oplus} + H_2O$$

18. (d) Phenol will undergo electrophilic substitution more readily than benzene.

19. (b,c) 

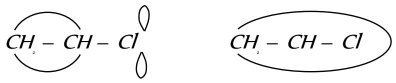
Di nitro fluoro benzene Di nitro phenol

20. (a) $AlCl_3$ is lewis acid *i.e.*, electron deficient compound. So it is electrophile.

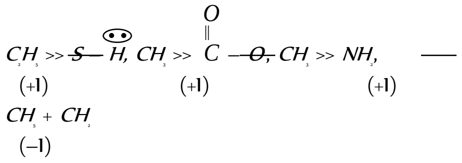
21. (d) CH_3-O^- is the strongest nucleophile which is capable of acting as donar of electon pair.

22. (a) The phenyl ring having $H - N<$ group is activated while another one is deactivated due to $\underset{\underset{O}{\|}}{-C-}$, so electrophilic aromatic bromination will occur at para position with respect to $H - N<$ group inactivated ring.

23. (d) The non reactivity of the chlorine atom in vinyl chloride may be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridization the $C - Cl$ bond will be a σ-bond and the two lone pairs of electron would occupy the other two sp^2 orbitals. This would leave a p-orbital containing a lone pair and this orbital could not conjugate with the π bond of the ethylenic link. Thus two M.O.S. will be required to accommodate these four π electrons. Further more since chlorine is more electronegative than carbon, the electron will tend to be found in the chlorine atom has now lost full control of the one pair and so, is less negative than it would have been had there been no conjugation. Since two carbon atoms have acquired a share in the lone pair, each atom acquires a small negative charge. Hence, owing to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group the lone pair must be localised again on the chlorine atom. This requires energy and so the chlorine is more firmly bound than has no conjugation occurred.



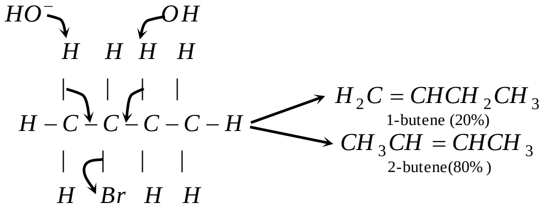
24. (a) Nucleophiles are those substances which can donate a pair of electrons. These can be neutral or negative. The nucleophilic power depends on the tendency of species to donate electrons. This is more, when an electron pushing group (+*I* group) is present. Among the alkyl groups, those having higher number of *C*-atoms will push more, hence ethyl > methyl.



25. (a) Conjugated acid of Cl^- is a stronger acid i.e., HCl.

26. (b) Saytzeffs product.

29. (b) If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according to the saytzeff rule, the main product is the most highly substituted alkene.



30. (d) Halogenation of alkanes takes place in presence of light (sunlight or UV) or at elevated temperature via free radical.

31. (d) All the given species undergo nucleophilic substitution reaction. This reactivity can be explained in terms of the nature of $C - X$ bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms.

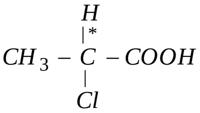
$$\overset{\delta^+}{-C} - \overset{\delta^-}{X}$$

32. (c) Increasing + I effect

$$(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$$

Structural and stereo isomerism

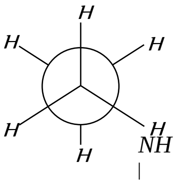
5. (b)

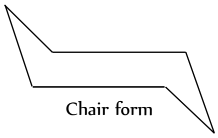


$$CH_3 - \overset{H}{\underset{Cl}{\overset{|*}{\underset{|}{C}}}} - COOH$$

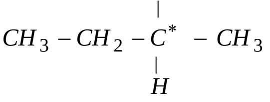
In this structure chiral carbon atom is present since it is optical active.

6. (b) In ethane staggard form and in cyclohexane chair form is more stable.




Chair form

7. (d)

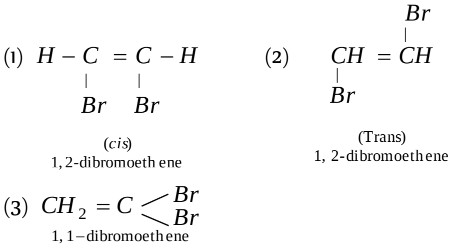


$$CH_3 - CH_2 - \overset{NH_2}{\underset{H}{\overset{|}{\underset{|}{C^*}}}} - CH_3$$

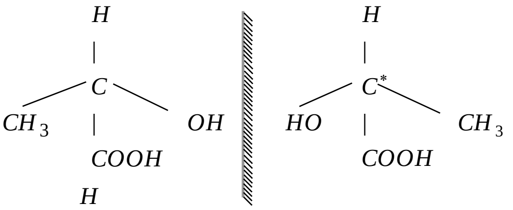
Chiral centre is present. Hence, it exists as optical isomers or enantiomorphs.

8. (c) In $C_6H_5CH_2CH_3$ chiral centre is absent.

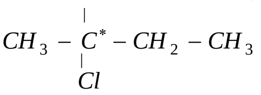
9. (c) $C_2H_2Br_2$ has three isomers.



10. (c) Lactic acid shows optical isomerism



11. (b)



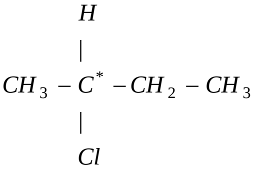
$$CH_3 - \overset{H}{\underset{Cl}{\overset{|}{\underset{|}{C^*}}}} - CH_2 - CH_3$$

2-Chlorobuta ne

because they contain chiral carbon atom.

12. (a)

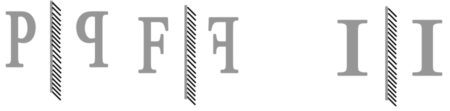
13. (a)



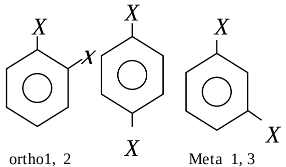
$$CH_3 - \overset{H}{\underset{Cl}{\overset{|}{\underset{|}{C^*}}}} - CH_2 - CH_3$$

In other compounds chiral carbon is absent.

14. (c) Ball is achiral where other objects are chiral because objects and their mirror images are non-super imposable

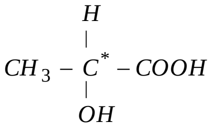

(a) (b) (d)

15. (c)



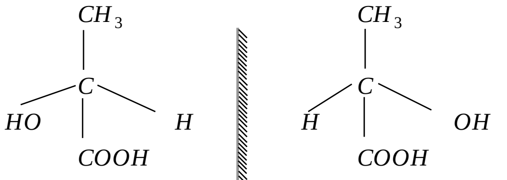
ortho1, 2 or 1, 6 Para 1, 4 Meta 1, 3 or 1, 5

17. (b)



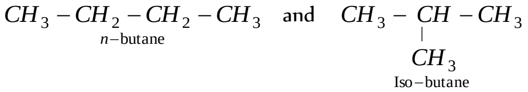
$CH_3-\overset{H}{\underset{OH}{C^*}}-COOH$

Only one chiral centre. Hence two optical isomers are possible.



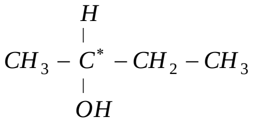
No. of optical isomer = 2 (where n = no. of chiral carbon) = $2^1=2$.

19. (a)



$\underset{n-\text{butane}}{CH_3-CH_2-CH_2-CH_3}$ and $\underset{\text{Iso}-\text{butane}}{CH_3-\underset{CH_3}{CH}-CH_3}$

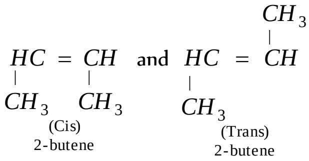
20. (d)



$CH_3-\overset{H}{\underset{OH}{C^*}}-CH_2-CH_3$ Chiral structure is that in which one carbon atom is attached to 4 different atoms or groups.

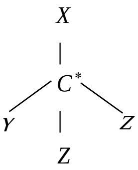
21. (b) $\underset{1-\text{butane}}{CH_3-CH_2-CH=CH_2}$ & $\underset{2-\text{butane}}{CH_3-CH=CH-CH_3}$

22. (a)



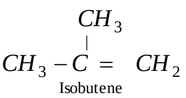
$\underset{\substack{\text{(Cis)}\\ \text{2-butene}}}{\underset{CH_3\quad CH_3}{HC=CH}}$ and $\underset{\substack{\text{(Trans)}\\ \text{2-butene}}}{\underset{CH_3}{HC}=\overset{CH_3}{CH}}$

23. (a) Four groups linked to carbon atom are different



25. (d) Five isomers of C_4H_8

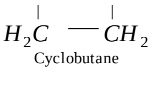
1.



$\underset{\text{Isobutene}}{CH_3-\overset{CH_3}{C}=CH_2}$

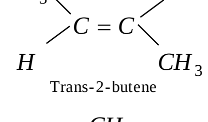
2. $\underset{1-\text{butene}}{CH_3CH_2-CH=CH_2}$

3.



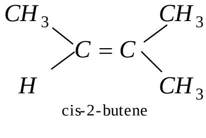
Cyclobutane

4.



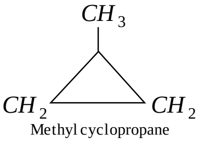
Trans-2-butene

5.



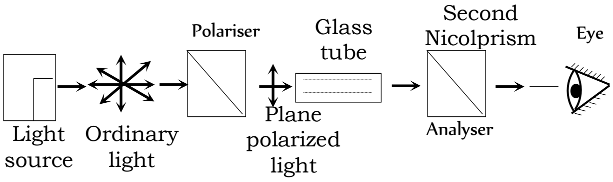
cis-2-butene

6.



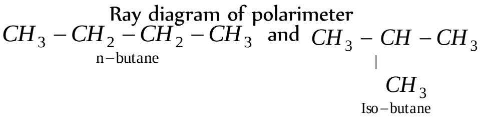
Methyl cyclopropane

26. (b) Polarimeter is an instrument used for measuring the optical rotation. It consists of two Nicol prisms, one called the polarizer (near the light source) and the other called the analyser (near the eye). In between the polarizer and analyser, a glass tube containing the solution of an optically active compound is placed.



Ray diagram of polarimeter

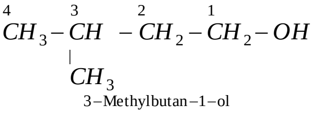
27. (d)



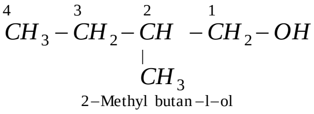
$\underset{n-\text{butane}}{CH_3-CH_2-CH_2-CH_3}$ and $\underset{\text{Iso}-\text{butane}}{CH_3-\underset{CH_3}{CH}-CH_3}$

28. (c) Metamerism is a special types of isomerism shown by secondary amines, ethers and ketones.

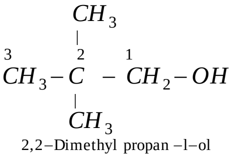
29. (c) $\underset{\text{Pentan-1-ol}}{CH_3-CH_2-CH_2-CH_2-CH_2-OH}$



$\underset{3-\text{Methylbutan}-1-\text{ol}}{\overset{4}{C}H_3-\overset{3}{\underset{CH_3}{C}}H-\overset{2}{C}H_2-\overset{1}{C}H_2-OH}$



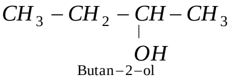
$\underset{2-\text{Methyl butan}-1-\text{ol}}{\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{\underset{CH_3}{C}}H-\overset{1}{C}H_2-OH}$



$\underset{2,2-\text{Dimethyl propan}-1-\text{ol}}{\overset{3}{C}H_3-\overset{\overset{CH_3}{2}}{\underset{CH_3}{C}}-\overset{1}{C}H_2-OH}$

30. (d) Position isomers :

$\underset{\text{Butan-1-ol}}{CH_3-CH_2-CH_2-CH_2-OH}$ and



$\underset{\text{Butan}-2-\text{ol}}{CH_3-CH_2-\underset{OH}{CH}-CH_3}$

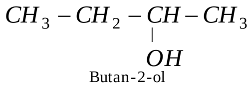
Functional isomers:

$\underset{\text{Butanol}}{CH_3CH_2CH_2-CH_2-OH}$ and $\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}$

Metamers: $\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}$ and $\underset{\text{Methyl propyl ether}}{CH_3-O-C_3H_7}$

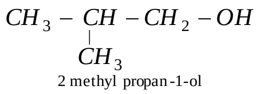
31. (a) 1. $\underset{\text{Butan-1-ol}}{CH_3-CH_2-CH_2-CH_2-OH}$

2.



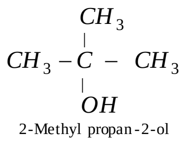
$\underset{\text{Butan-2-ol}}{CH_3-CH_2-\underset{OH}{CH}-CH_3}$

3.



$\underset{\text{2 methyl propan-1-ol}}{CH_3-\underset{CH_3}{CH}-CH_2-OH}$

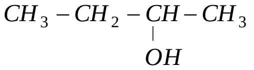
4.

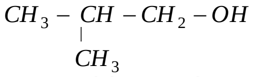


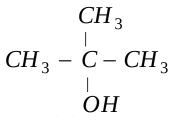
$\underset{\text{2-Methyl propan-2-ol}}{CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3}$

32. (d) $C_4H_{10}O$ have six isomers are possible

1. $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2-OH}$

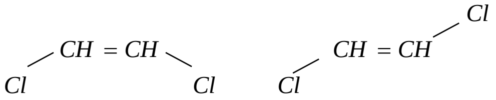
2. 
$CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_3$
Butan-2-ol

3. 
$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - OH$
2-Methyl propan-1-ol

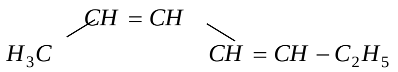
4. 
$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - CH_3$
2−Methyl-propan-2-ol

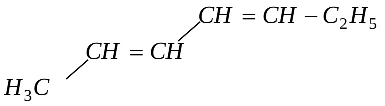
5. $CH_3 - O - C_3H_7$
Methyl propyl ether

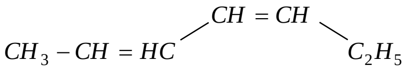
6. $C_2H_5 - O - C_2H_5$
Diethyl ether

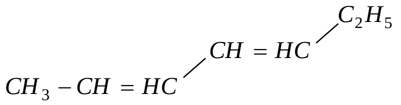
33. (b) 
(*cis*) (*trans*)

34. (a) $\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH} = \overset{5}{CH} - \overset{6,7}{C_2H_5}$

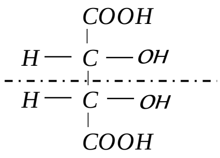
1. 
(*cis*)

2. 
(*trans*)

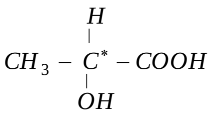
3. 
(*cis*)

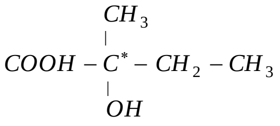
4. 
(*trans*)

36. (a) Molecular symmetry


$$\begin{array}{c} COOH \\ | \\ H - C - OH \\ H - C - OH \\ | \\ COOH \end{array}$$

Mesotartaric acid is optically inactive due to internal compensation *i.e.* the effect one half of the molecule is neutralized by other.

37. (b) 
$CH_3 - \overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C^*}} - COOH$ * chiral centre is present.

38. (b) 
$COOH - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C^*}} - CH_2 - CH_3$

One chiral centre. Therefore two forms are possible.

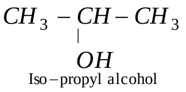
39. (c) Optical isomerism and geometrical isomerism.

40. (d) (a) $CH_3CH_2CH_2COOH\,(C_4H_8O_2)$

(b) $CH_3CH_2 - COOCH_3\,(C_4H_8O_2)$

Diethyl ether $C_2H_5 - O - C_2H_5$ is position isomer and not stereoisomer.

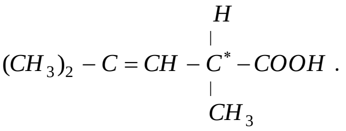
41. (c) $C_2H_5 - O - C_2H_5$ and $CH_3 - O - C_3H_7$ are metamers.

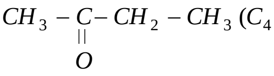
42. (a) $\underset{\text{n−propyl alcohol}}{CH_3 - CH_2 - CH_2 - OH}$ and  $\underset{\text{Iso−propyl alcohol}}{CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3}$

are position isomers of each other.

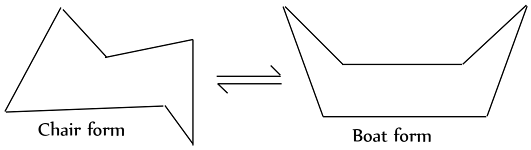
44. (a) $R - N \overset{=}{=} C$ and $R - C \equiv N$ are functional isomers.

45. (b) Optical isomerism because chiral centre is present


$(CH_3)_2 - C = CH - \overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C^*}} - COOH$.

46. (d) Butanone  $CH_3 - \underset{\underset{O}{||}}{C} - CH_2 - CH_3\,(C_4H_8O)$ is not an isomer of $C_2H_5 - O - C_2H_5\,(C_4H_{10}O)$

47. (d) Chair and boat form differ in energy by 44 *kJ/mol.*



48. (b) $CH_3 - O - CH_2 - CH_3$ and $CH_3CH_2CH_2 - OH$

ethylmethyl ether and propylalcohol are functional isomers.

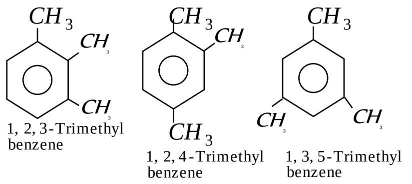
49. (c) $CH_3 - CH_2 - CH_2^{-}O - C_2H_5$
Ethoxy propane

$CH_3 - CH_2 - CH_2 - O - C_2H_5$
Propoxy ethane

Both are same compounds.

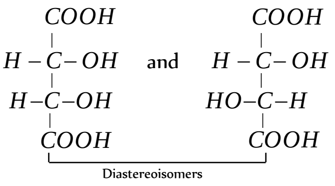
50. (a) $CH_3 - CO - CH_3$ and $CH_3 - CH_2 - CHO$ are functional isomers.

51. (b) Three isomers are possible

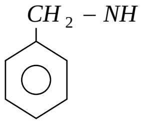


52. (d) Diastereoisomers – Optical isomers which are not mirror images of each other.

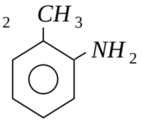
e.g.


$$\underbrace{\begin{array}{c} COOH \\ | \\ H - C - OH \\ | \\ H - C - OH \\ | \\ COOH \end{array} \quad \text{and} \quad \begin{array}{c} COOH \\ | \\ H - C - OH \\ | \\ HO - C - H \\ | \\ COOH \end{array}}_{\text{Diastereoisomers}}$$

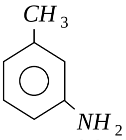
53. (b) C_7H_9N has 5 isomers



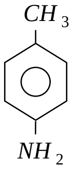
Benzyl amine



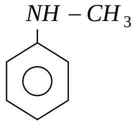
O–Methyl aniline



m–methyl aniline



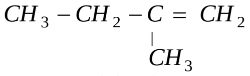
p–methyl aniline



n–methyl aniline

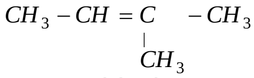
54. (d) (1) $CH_3-CH_2-CH_2-CH=CH_2$ Pent -1-ene

(2) $CH_3-CH_2-CH=CH-CH_3$ Pent -2-ene

(3) 

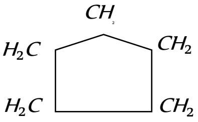
$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

2–Methyl–1–butene

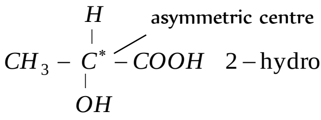
(4) 

$$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$$

2–Methyl–2–butene

(5) 

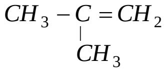
Cyclopentane

55. (d) 

$$CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C^*}}}}-COOH$$

asymmetric centre

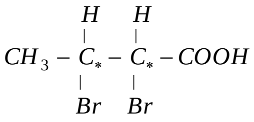
2–hydroxy propanoic acid (lactic acid)

58. (d) 

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

2-methyl propene does not show geometrical isomerism.

59. (b) Conformers - Conformation arises because of free rotation around $C-C$ bond axis.

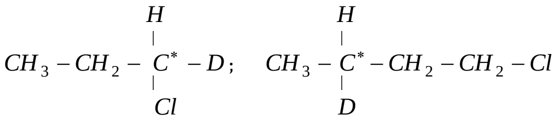
60. (d) 

$$CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C_*}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C_*}}}}-COOH$$

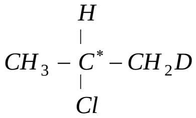
Number of enantiomers = 2^n (n = asymmetric Carbon atom) = 2^2 = 4.

61. (b) $C_6H_5C\equiv N$ and $C_6H_5N\overset{\rightarrow}{=}C$ are functional isomers.

62. (a) $DCH_2-CH_2-CH_2-Cl$ Others are chiral

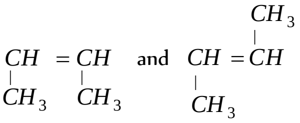


$$CH_3-CH_2-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C^*}}}}-D;\quad CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle D}{\underset{|}{C^*}}}}-CH_2-CH_2-Cl$$

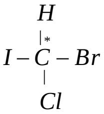


$$CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C^*}}}}-CH_2D$$

63. (d) Cis and trans 2-butene are geometrical isomers.



$$\underset{\displaystyle CH_3}{\underset{|}{CH}}=\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{ and }\underset{\displaystyle CH_3}{\underset{|}{CH}}=\overset{\displaystyle CH_3}{\overset{|}{CH}}$$

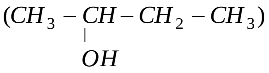
64. (d) 

$$I-\overset{\displaystyle H}{\overset{|*}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-Br$$

A carbon atom which is attached to four different atoms or groups is called a chiral or asymmetric carbon atom. such a carbon atom is often marked by an asterisk.

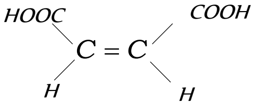
65. (b) $\underset{\text{Cyanide}}{R-C\equiv N}$ and $\underset{\text{Isocyanide}}{R-N\overset{\rightarrow}{=}C}$ are functional isomers.

66. (b) Glucose and fructose have similar molecular formula with difference of functional group, so they are functional isomers.

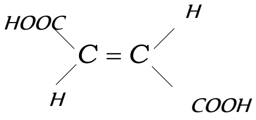


67. (b) 2-butanol $(CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3)$ is optically active because it has asymmetric carbon atom.

69. (d) Ethane has all single (σ) bonds so there is minimum resistance in bond rotation.

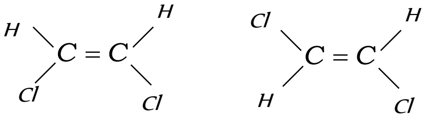
70. (a) 

Maleic acid (cis isomer)

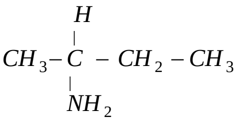


Fumaric acid (trans isomer)

71. (a) $ClHC=CHCl$ two structures are possible



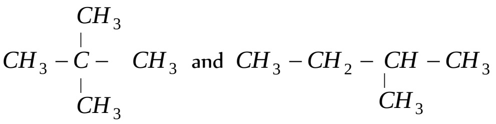
Geometrical isomerism

72. (c) 

$$CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle NH_2}{\underset{|}{C}}}}-CH_2-CH_3$$

Secondary butyl amine is optically active.

73. (c) Neopentane and isopentane are chain isomers.



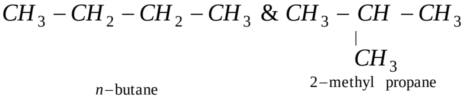
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3\text{ and }CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

75. (a) Due to single bond there is no hindrance

77. (a) Only 1-phenyl-2-butene will exhibit *cis-trans* isomerism.

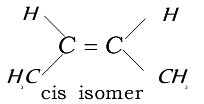
79. (a) Geometrical isomerism is not possible in propene.

80. (a) Two isomeric forms are possible for 2-methyl propane.

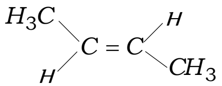


$$\underset{n\text{–butane}}{CH_3-CH_2-CH_2-CH_3}\ \&\ \underset{\text{2–methyl propane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3}$$

84. (d) Restricted rotation is essential condition for geometrical isomerism.

88. (a) 

cis isomer

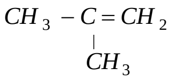
and 

Trans isomer

89. (b) Three isomeric structures are possible for C_4H_8

$H_2C=CH-CH_2-CH_3$

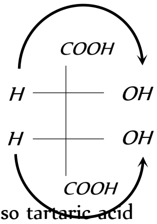
$CH_3-CH=CH-CH_3$



$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

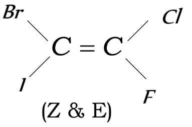
92. (a) Enantiomers have same chemical properties but different physical properties.

93. (a) Meso isomer have two achiral carbon with opposite spin so it becomes optically inactive

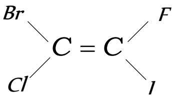


Meso tartaric acid

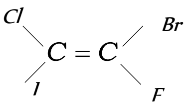
95. (d)



(Z & E)



(Z & E)



(Z & E)

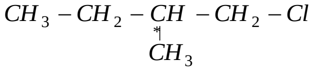
96. (b) Due to formation of the plane of symmetry by the syn addition of hydrogen in the triple bond, the compound formed is optically inactive.

101. (b) Racemic mixture is combination of *d* and *l* isomers.

102. (c) $Cl_2C=CH-CH_2-CH_2-CH_2$. It can't show geometrical isomerism due to unsymmetrical alkene.

103. (b) Geometrical isomerism.

104. (b)

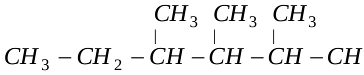


$CH_3-CH_2-\underset{\underset{CH_3}{|^*}}{CH}-CH_2-Cl$

105. (a) Functional isomerism

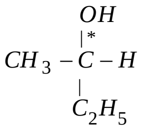
109. (b) Non superimposible on its mirror image.

112. (d)



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$, it is a chiral compound.

114. (d)



$CH_3-\overset{\overset{OH}{|^*}}{\underset{\underset{C_2H_5}{|}}{C}}-H$

In this structure chiral carbon is present that is why it is optically active.

115. (b) 2-chloro butane will be optically active.

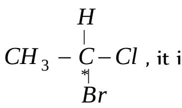
118. (b) Structures are mirror images of each other which are non super impossible so they are enantiomers.

120. (d) Both have one chiral carbon atom hence racemic mixture will be obtain

121. (b) Structure have 3-different atoms and group so it is unable to show geometrical isomerism

122. (c) Metamerism is shown by the different arrangement of alkyl group about functional group.

124. (b)

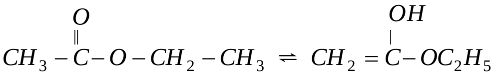


$CH_3-\overset{\overset{H}{|}}{\underset{\underset{Br}{|^*}}{C}}-Cl$, it is a chiral compound.

126. (c) CH_3-O-CH_3 and C_2H_5OH are functional isomers.

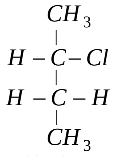
127. (c) Both are enantiomer.

128. (d) $CH_3COOC_2H_5$ shows tautomeric isomerism.



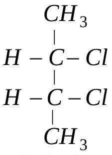
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3 \rightleftharpoons CH_2=\overset{\overset{OH}{|}}{C}-OC_2H_5$

129. (b)



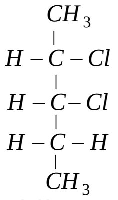
$\begin{array}{c}CH_3\\|\\H-C-Cl\\|\\H-C-H\\|\\CH_3\end{array}$

2 chlorobutane



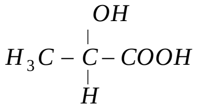
$\begin{array}{c}CH_3\\|\\H-C-Cl\\|\\H-C-Cl\\|\\CH_3\end{array}$

2, 3 dichlorobutane



$\begin{array}{c}CH_3\\|\\H-C-Cl\\|\\H-C-Cl\\|\\H-C-H\\|\\CH_3\end{array}$

2, 3 dichloropentane

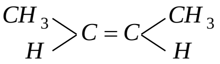


$H_3C-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-COOH$

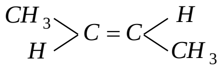
2 hydroxy propanoic acid

130. (d) Gaseous density of both ethanol and dimethyl ether would be same under identical condition of temperature and pressure while the rest of these three properties vapour pressure, boiling point and heat of vaporization will differ as ethanol has hydrogen bonding where as ether does not.

132. (a)



cis 2 butene



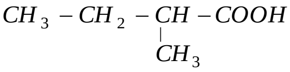
Trans 2 butene

Cis-trans isomerism shown by compound which have double or triple bond by which they restrict their rotation, since 2 butyne have no hydrogen on triple bonded carbon.

$CH_3-C\equiv C-CH_3$ [It does not show cis-trans]

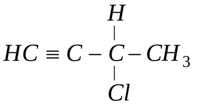
2 butyne

133. (d) Because it contain asymmetric carbon atom.



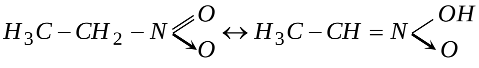
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-COOH$

135. (b)

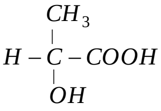


$HC\equiv C-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$ shows optical isomerism because of molecule is unsymmetrical. That is called chiral.

136. (c) Nitroalkanes exhibit tautomerism. In it, $\alpha-H-$ atom is labile and form nitrolic acid.

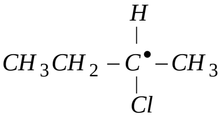


137. (b)



$H-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-COOH$ shows optical isomerism due to presence of asymmetric carbon atom.

138. (a) 2-chloro butane has a chiral carbon atom, hence only it will show optical activity and will possess two enantiomers (one chiral carbon atom).



$CH_3CH_2-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C^{\bullet}}}-CH_3$

139. (b) C_4H_7Cl is a monochloro derivative of C_4H_8 which itself exists in three isomeric forms.

(i) $CH_3-CH_2-CH=CH_2$: Its possible mono-chloro derivatives are :

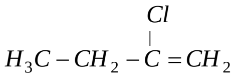
$CH_3-CH_2-CH=CH-Cl$

2 isomers : cis and trans forms

$CH_3-\underset{\underset{Cl}{|}}{\overset{\bullet}{C}H}-CH=CH_2$

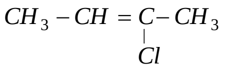
optically active (exists in two forms)

$ClCH_2-CH_2-CH=CH_2$ (one form)



$H_3C-CH_2-\overset{\overset{Cl}{|}}{C}=CH_2$ (one form)

(ii) $CH_3-CH=CH-CH_3$: Its possible monochloro derivatives are :

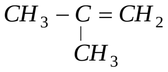


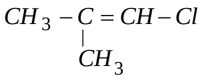
$CH_3-CH=\underset{\underset{Cl}{|}}{C}-CH_3$

Exists in two geometrical forms

$CH_3-CH=CH-CH_2Cl$

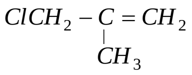
Exists in two geometrical forms

(iii)  $CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$: Its possible monochloro derivatives are



$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-Cl$

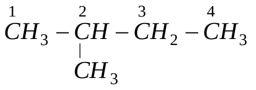
Only one form



$ClCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$

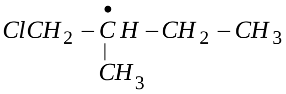
Only one form

Thus, the total acylic isomers forms of C_4H_7Cl are 12.

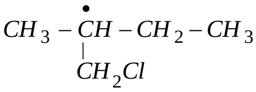
140. (d) 

$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$

Its monochloro derivatives are as follows :

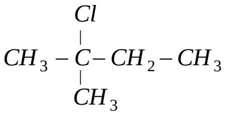
(i) 

$ClCH_2-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}H}-CH_2-CH_3$

or 

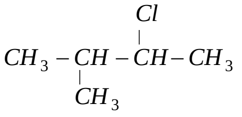
$CH_3-\underset{\underset{CH_2Cl}{|}}{\overset{\bullet}{C}H}-CH_2-CH_3$

It will exist as enantiomeric pair (*d* and *l*-forms)

(ii) 

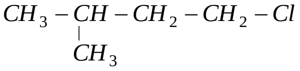
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CH_3$

no asymmetric *C* atom

(iii) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{CH}-CH_3$

It will exist as enantiomeric pair (*d*- and *l*-forms)

(iv) 

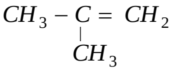
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-Cl$

No asymmetric carbon atom

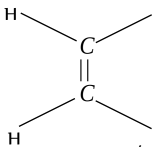
Hence, only two enantiomeric pairs will be obtained by the monochlorination of 2-methylbutane.

141. (d) When isomers have the structural formula but differ in the relative arrangement of atoms or groups in space with in the molecule, these are known as sterioisomers and the phenomenon as sterio isomerism. Stereoisomerism is of three types (i) Geometrical isomerism (ii) Optical isomerism (iii) Conformational isomerism.

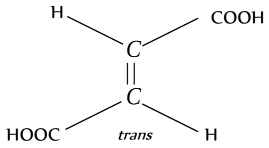
144. (a) $CH_3=CH-CH_2-CH_3$; $CH_3-CH=CH-CH_3$;



$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

145. (c) 

and

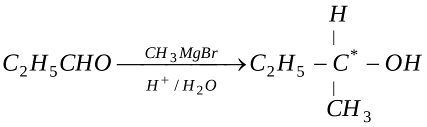


146. (d) *Trans* configuration is more stable than *cis* configuration because in *cis*-configuration the *H* groups are thrown closely enough together to cause crowding or repulsion. Again between 1,2-and 1,3-configurations, in 1-3, the *OH* groups are placed further apart to minimise the repulsion. Hence, more stable is 1,3-configuration.

147. (a) Chirality of carbon compound is because of its tetrahedral nature of carbon.

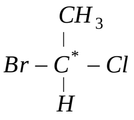
148. (c) $\underset{\text{1-chloro-2-nitroethene}}{O_2NHC=CHCl}$

For highly substituted alkenes *E* and *Z* system of nomenclature is used, which is based on a priority system developed by Cahn, Ingold and Prelog.

149. (b) 

$C_2H_5CHO\xrightarrow[H^+/H_2O]{CH_3MgBr}C_2H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C^*}}-OH$

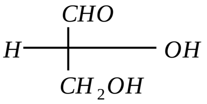
C^*-chiral carbon as all the four valencies are attached with different substituents or groups.

150. (b) 

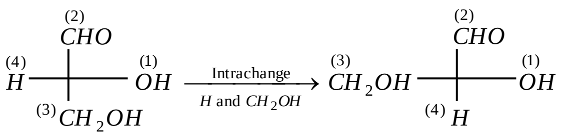
$Br-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C^*}}-Cl$ * asymmetric or chiral carbon

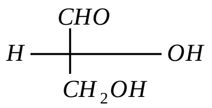
All the four valencies of carbon are satisfied with different atoms/substituents.

151. (c) The configuration in which, OH group are on right side, H-atom are on left side, CHO group are on upper side & CH_2OH are on lower side found in fischer projection known as D-configuration.

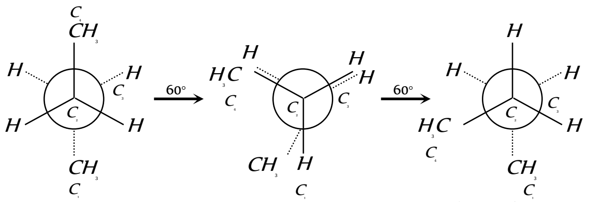


D-glyceraldehyde



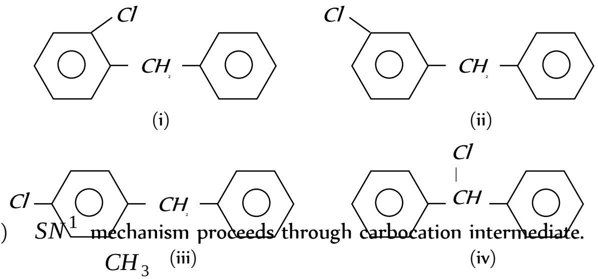
or 

Critical Thinking Questions

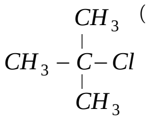
1. (c) 

Gauche conformation

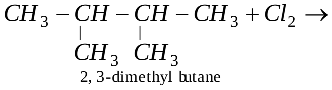
2. (d) Only four structural isomers are possible for diphenyl methane.



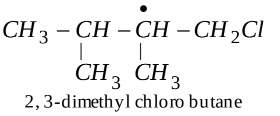
3. (c) SN^1 mechanism proceeds through carbocation intermediate.


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$ provides stable carbocation intermediate because it has tertiary carbon.

4. (e)

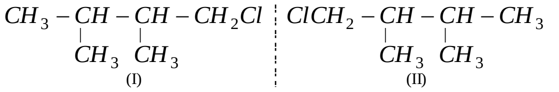

$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3+Cl_2\rightarrow$

2, 3-dimethyl butane

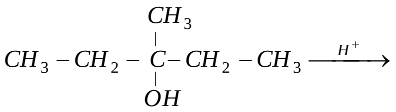

$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{\overset{\bullet}{CH}}-CH_2Cl$

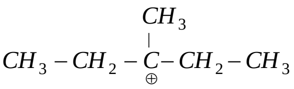
2, 3-dimethyl chloro butane

Due to the presence of chiral carbon it shows the optical activity and its mirror image are non superimposable so it shows one enantiomer pair.


$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2Cl$ (I) ⋮ $ClCH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$ (II)

5. (a)

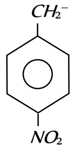

$CH_3-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_2-CH_3\xrightarrow{H^+}$


$CH_3-CH_2-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-CH_3$

The more stable carbocation is generated thus more easily it will be dehydrated.

6. (b) This option is not characteristics of free radical chain reaction.

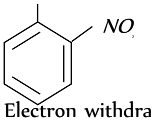
7. (c) Due to NO_2 group in benzene ring,



is most stable carbanion.

8. (d) Dissociation of proton from $CH_3-\overset{+}{N}H_3Cl^-$ is very difficult due to $-I$ effect of Cl^- and N^+ while in C_6H_5OH due to resonance stabilization of phenoxide ion proton eliminate easily similarly due to *H*-bonding in $C_6H_5CH_2OH$ it can be eliminate and $CH_3C\equiv CH$ show acidic character by triple bond by which proton can be dissociate.

9. (b)



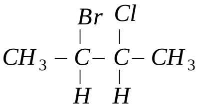
Electron withdrawing group increases acidic character due to –*I* and –*R* effect of NO_2 hence orthonitrophenol is most acidic.

10. (d) Halogenation on alkene occurs by electrophilic addition.

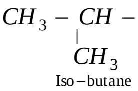
11. (c) The number of possible optical isomers $=2^n$

(where '*n*' is the number of chiral *c*-atoms) $=2^3=8$

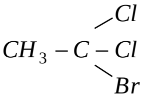
12. (c) 2-bromo, 3-chloro-butane has 2 chiral carbon atoms, hence has $2^2=4$ optical isomers.

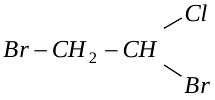

$CH_3-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$

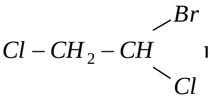
13. (a) $CH_3-CH_2-CH_2-CH_3$, *n*–Butane


$CH_3-\underset{CH_3}{CH}-CH_3$ Iso – butane

14. (b) $C_2H_3Cl_2Br$ three isomers are possible

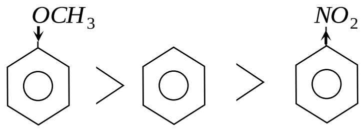

1-bromo-1, 1-dichloroethane


1-bromo-2,2-di-chloroethane


1-bromo-1, 2-dichloroethane

15. (c) *D*(+)-tartaric acid has positive optical rotation and is derived from *D* (+) glyceraldehyde.

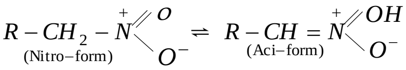
16. (c) I > II > III



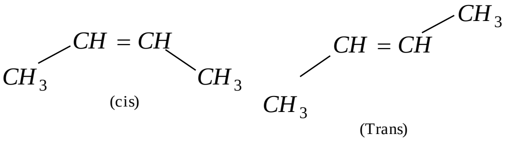
Methoxy group is electron releasing it increases electron density of benzene nucleus while $-NO_2$ decreases electron density of benzene.

17. (c) Due to resistance benzyl carbonium ion is most stable.

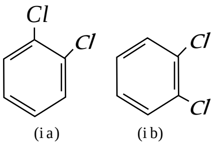
18. (d)



19. (b)

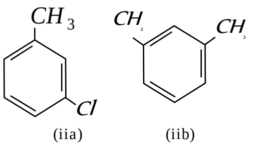


20. (d)



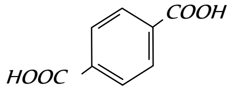
Both 1, 2-dichloro benzene

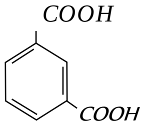
Hence, identical compounds.



Both, 1, 3-dimethyl benzene

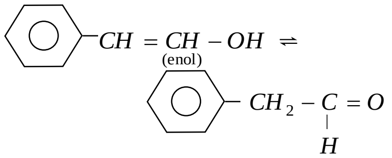
Hence, identical compounds.


(iiia)

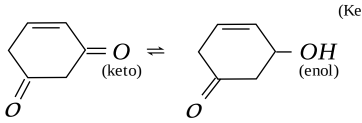

(iiib)

(iiia) and (iiib) are position isomers.

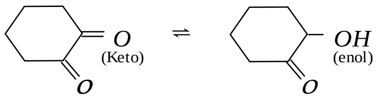
21. (a,c,d) (a)



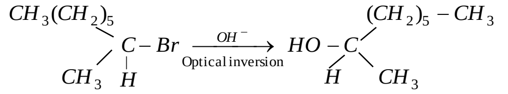
(c)



(d)



22. (c)



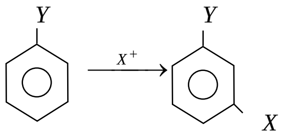
In this reaction inversion of configuration takes place this is called optical inversion. It is an example of SN^2 reaction (Bimolecular Nucleophillic Substitution).

23. (b) This option shows eclipsed form of ethane.

24. (c) 2^{nd} and 4^{th} forms of ethane are staggered.

25. (b) $(CH_3)_3C^+$ 3° carbonium ion is most stable.

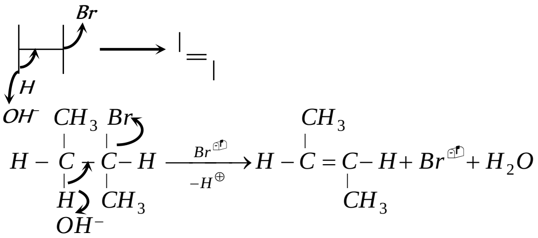
26. (a)



m–isomer
(>60%)

$Y = –COOH$ because it is meta directing group while $–NH_2$. $–OH$ and $–Cl$ are O and P directing groups.

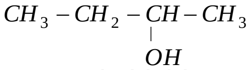
27. (a)



28. (c) $C_4H_{10}O$ have 7 isomers out of which 4 are alcohols and 3 are ethers.

1. $CH_3 – CH_2 – CH_2 – CH_2 – OH$,
n–butyl alcohol

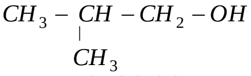
2.



$CH_3 – CH_2 – \underset{OH}{\underset{|}{CH}} – CH_3$

Sec –butyl alcohol

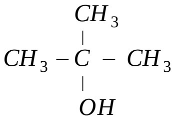
3.



$CH_3 – \underset{CH_3}{\underset{|}{CH}} – CH_2 – OH$

Isobutyl alcohol

4.



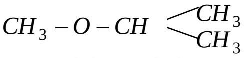
$CH_3 – \overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}} – CH_3$

Ter– buty – alcohol

5. $CH_3 – CH_2 – O – CH_2 – CH_3$
Diethyl ether

6. $CH_3 – O – CH_2 – CH_2 – CH_3$
Methyl propyl ether

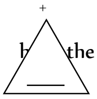
7.



Methyl isopropyl ether

29. (a) According to Huckel rule for aromaticity the molecule must be planar, cyclic system having delocalised $(4n + 2)\pi$ electron where n is an integer equal to 0, 1, 2, 3, thus the aromatic comp. have delocalised electron cloud of

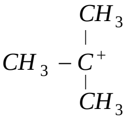
2, 6, 10 or 14π electron cyclopropenyl cation h the 2π electron ($n = 0$) so it is aromatic.



30. (d) $–COOH$ group is a deactivating group, hence benzoic acid is less reactive towards electrophilic substitution than phenol.

31. (c) In the triphenyl methyl carbonium ion the π electrons of all the three benzene rings are delocalised with the vacant p-orbital of central carbon atom. So, it is resonance stabilised. It is the most stable of all the carbonium ions given

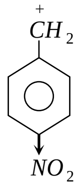
The ion



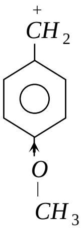
$CH_3 – \overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C^+}}}}$

is stabilised by hyperconjugation, a second order resonance.

32. (b)

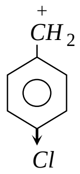


Nitro-group is electron withdrawing therefore decreases stability.



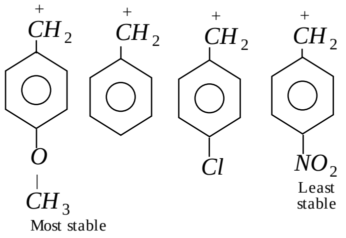
Methoxy group is electron releasing.

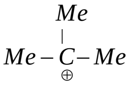
Therefore increases stability by donating electron.



Chlorine is also electron withdrawing but its effect is less than $-NO_2$ group.

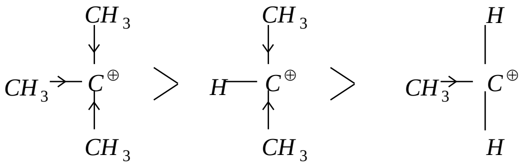
Hence, correct order of stability.

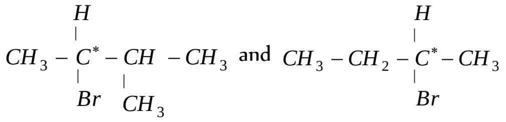


33. (b) 3° alcohols  $Me-\underset{\oplus}{\overset{\overset{Me}{|}}{C}}-Me$ is most stable carbocation

34. (b) Due to the increasing no. of hyperconjugative structures free radical stabilise following as $3° > 2° > 1°$.

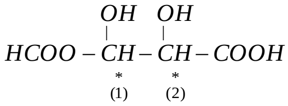
35. (c) $3° > 2° > 1°$



36. (b,c)  $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C^*}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ and $CH_3-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C^*}}-CH_3$

37. (b) $\underset{\text{Diethyl thioether}}{C_2H_5-S-C_2H_5}$ and $\underset{\text{Methyl propyl thioether}}{CH_3-S-C_3H_7}$

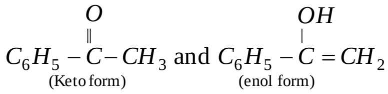
are metamers.

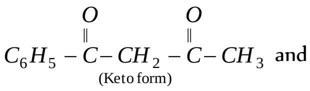
38. (b)  $HCOO-\underset{\underset{(1)}{*}}{\overset{\overset{OH}{|}}{CH}}-\underset{\underset{(2)}{*}}{\overset{\overset{OH}{|}}{CH}}-COOH$

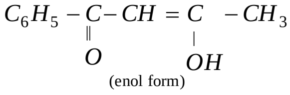
Two carbon atoms in the molecule are asymmetric.

39. (a,b,d) $CH_3\ddot{N}H_2, R-\underset{..}{\ddot{O}}-, CH_3-Mg-\underset{..}{\ddot{Br}}:$ are nucleophiles due to presence of lone pairs.

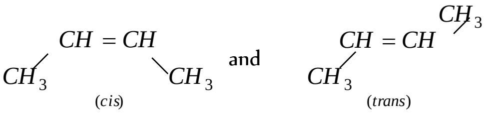
40. (c) CH_3^- has the highest nucleophilicity.

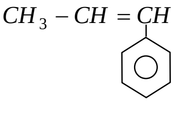
41. (c,d)  $\underset{\text{(Keto form)}}{C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3}$ and $\underset{\text{(enol form)}}{C_6H_5-\overset{\overset{OH}{|}}{C}=CH_2}$

 $\underset{\text{(Keto form)}}{C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$ and

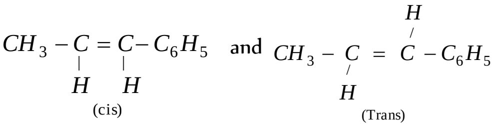
 $\underset{\text{(enol form)}}{C_6H_5-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CH_3}$

42. (a,c) 2-butene





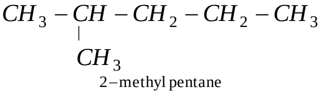
1-phenyl propene

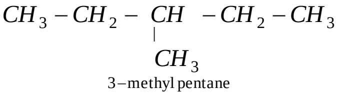


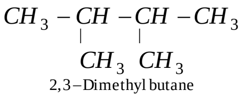
43. (c) CH_3CN behaves both as nucleophile and electrophile.

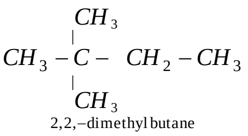
44. (c) 2^n, n = no. of asymmetric carbon atoms.

45. (b) 1. $\underset{\text{n−hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$

2.  $\underset{\text{2−methyl pentane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3}$

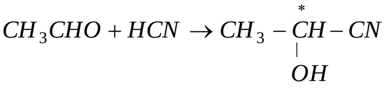
3.  $\underset{\text{3−methyl pentane}}{CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3}$

4.  $\underset{\text{2,3−Dimethyl butane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3}$

5.  $\underset{\text{2,2,−dimethyl butane}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3}$

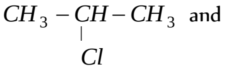
46. (c) Stability of carbanions increase with increase in *s*-character of hybrid orbitals of carbon bearing charge, hence correct order is : $sp^3 < sp^2 < sp$.

47. (b) $\underset{1.20\,Å}{C_2H_2} < \underset{1.34\,Å}{C_2H_4} < \underset{1.39\,Å}{C_6H_6} < \underset{1.54\,Å}{C_2H_6}$

48. (d)  $CH_3CHO + HCN \rightarrow CH_3-\underset{\underset{OH}{|}}{\overset{*}{C}H}-CN$

(Both *d* and *l* forms are obtained) Hence, product will be a racemic mixture.

49. (d) Molecule 'A' is benzene because in benzene bond length is between single and double bond.

50. (a) Two isomers  $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$ and

$CH_3-CH_2-CH_2Cl$ are possible for C_3H_7Cl.

Assertion & Reason

1. (a) It is fact that aniline is better nucleophile than anilium ion. Anilium ion contain +*ve* charge, which reduces the tendency to donate lone pair of electron $\underset{\text{Aniliumion}}{C_6H_5NH_3^+}$.

Therefore, both assertion and reason are true.

2. (b) Neopentane is isomer of pentane and neopentane forms only one substitution product. Both assertion and reason are true but reason is not a correct explaination of assertion. Neopentane forms mono substituted product due to presence of four identical methyl groups present on carbon atom.

3. (c) The assertion that *trans-2* butene reacts with Br_2 to product meso-2, 3-dibromobutane is correct but it does not involve *syn*-addition of Br_2.

4. (d) Here both assertion and reason are incorrect because *cis*-1, 3-dihydroxy cyclohexane exist in chair conformation and in chair conformation hydrogen bonding is present.

5. (a) Hydroxy ketones are not directly used in Grignard reagent. Grignard reagents are very reactive. Therefore, they react with hydroxyl group. Here both are correct.

6. (a) The assertion that on keeping benzyl bromide in acetone water it produces benzyl alcohol is correct. Because $C_6H_5CH_2Br$ hydrolysed to produce $C_6H_5CH_2OH$. This conversion is of SN^2 mechanism.

7. (b) Catenation property of carbon is primarily due to its small size. Electronic configuration and unique strength of carbon-carbon bonds.

8. (e) Olefins are unsaturated hydrocarbons containing two hydrogen atoms less than the corresponding paraffin *i.e.* there is one double bond between two carbon atoms in their molecules and they have the general formula C_nH_{2n}.

9. (b) Less reactivity of saturated hydrocarbons are due to presence of single bonds between carbon atoms.

10. (b) Glucose is insoluble in ether.

11. (a) An alkyl group attached to the positively charged carbon of a carbonium ion tends to release electrons towards that carbon; thus the positive charges gets dispersed as the alkyl group becomes some what positively charged itself. More the number of alkyl groups, the greater is the dispersal of positive charge and therefore more easily it will be formed.

12. (b) Heterolytic fission occurs when the two atoms differ considerably in their electronegativities and shared pair of electrons is carried by more electronegative atom.

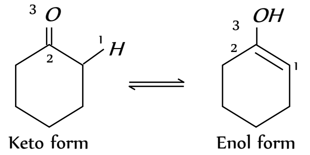
13. (d) The order of reactivity of carbonium ions is $1° > 2° > 3°$.

Carbon atom in carbonium ion is in sp^2 state of hybridisation. The three hybridized orbitals lie in the same plane and are involved in the formation of three σ bonds with three atoms or groups while the unhybridised *p*-orbital remains vacant.

14. (b) Since free radicals contain odd electrons, so they are short lived and they readily try to pair up the odd electrons to form neutral molecules, that is why they are highly reactive.

15. (b) Each carbon atom in ethylene is attached to two hydrogen atoms by single covalent bonds and to another carbon atoms by a double bond. Since each carbon is attached to three other atoms, it uses sp^2 hybrid orbitals and an unhybridised p_Z orbital to form its bond. Each $C-H$ bond is a σ bond resulting from the overlap of $1s$ orbital of hydrogen atom and sp^2 orbital of a carbon atom. One $C-C$ bond results from the linear overlap of sp^2 orbitals one from each carbon atom. One π bond results from the lateral overlap of two unhybridised p_Z orbitals, one from each carbon atom.

16. (a) In cyclohexanone keto enol tautomerism is as follows



17. (e) The staggered form is more stable than the eclipsed form because the potential energy of staggered form in which the bond pairs of two carbons are far away from each other is minimum. Also the *H*-atoms are as far apart as possible and non bonded interaction between them is maximum. In occupied form, the *H*-atom are very close and so the increased overlap between them non-bonded orbitals is repulsive. That is why staggered form is more stable than eclipsed form.

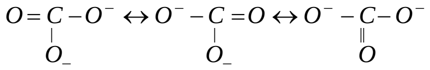
18. (b) Trans isomer is more stable than cis isomer because in cis isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups makes the cis isomer less stable than the trans isomer in which the bulky groups are far apart. (They are on the opposite side of the double bond).

19. (e) 1, 2-propadiene is not optically active because the terminal sp^2-hybridised carbons have the same atoms *i.e.* *H*-atoms. As a result, it has a plane of symmetry passing through the three carbon atoms and hence the molecule is optically inactive.

20. (b) Lactic acid is a chiral molecule because it has a chiral carbon atom or asymmetric carbon atom and is therefore optically active.

21. (e) Resonance structures contain the same number of unpaired electrons.

22. (b) CO_3^{2-} shows resonance and thus all the three bonds are of identical bond length.



$$O=\underset{\underset{O^-}{|}}{C}-O^- \leftrightarrow O^- -\underset{\underset{O^-}{|}}{C}=O \leftrightarrow O^- -\underset{\underset{O}{\|}}{C}-O^-$$