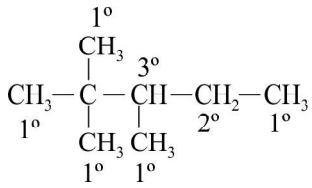
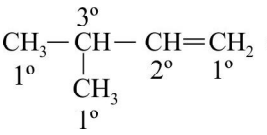
SOLUTIONS

Module - 3 / JEE-2022

IN-CHAPTER EXERCISES	Chemistry	Introduction to Organic Chemistry

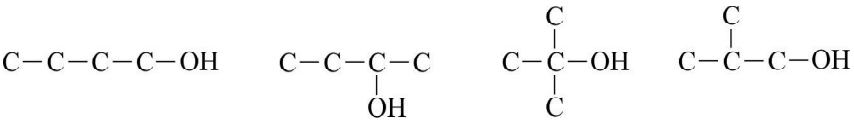
EXERCISE-A

1. **i.(B)**  = 18 Hydrogen

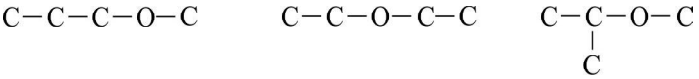
ii.(BD)  = 5 Carbon, 10 Hydrogen

iii.(BC) In bond line representation carbon, hydrogen atom and C–H bonds are not shown but C–C bonds are shown by lines.

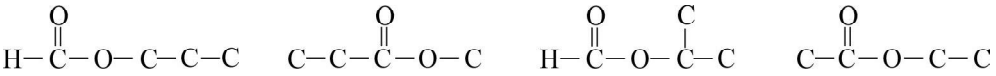
iv.(C) Possible alcohols are



Possible ethers are

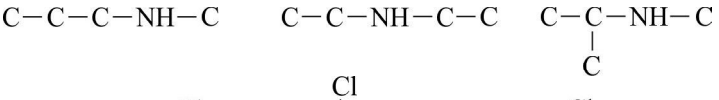


v.(D)

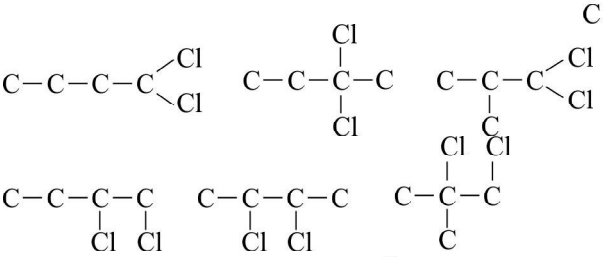


vi.(AC) In conjugate diene π bonds are present at alternate positions.

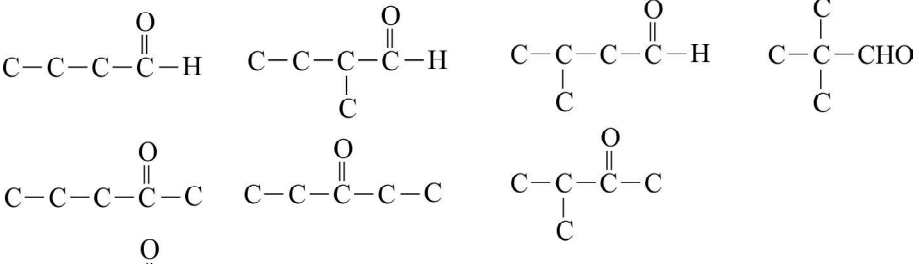
vii.(C)



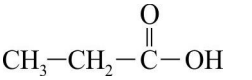
viii.(D)



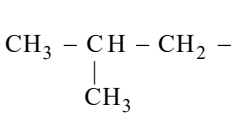
ix.(A)

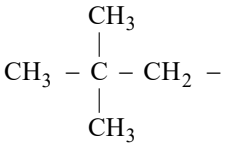


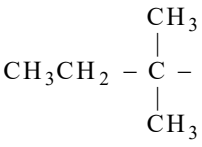
x.(C)

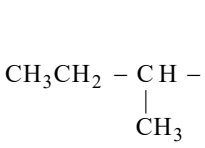


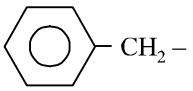
because only acid satisfy this formula $C_nH_{2n}O_2$.

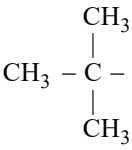
2. **(i)** 

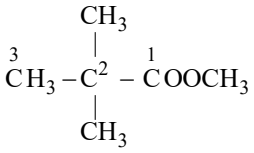
(ii) 

(iii) 

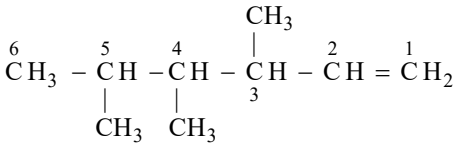
(iv) 

(v) 

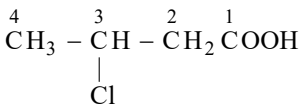
(iv) 

3. **(i)** 

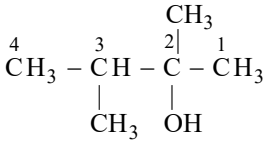
(Methyl) 2, 2 - Dimethyl propanoate

(ii) 

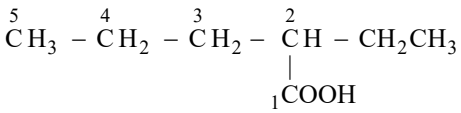
3, 4, 5 - trimethylhex - 1 - ene

(iii) 

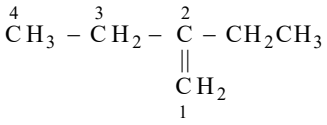
3 - chlorobutanoic acid

(iv) 

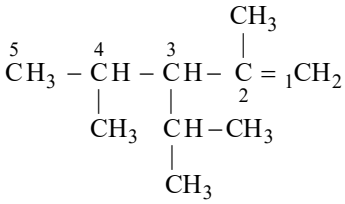
2, 3 - Dimethyl butan - 2 - ol

(v) 

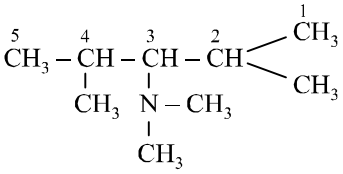
2 - Ethyl pentanoic acid

(vi) 

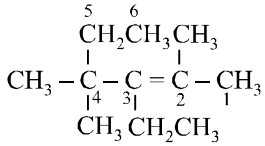
2 – Ethyl but - 1 - ene

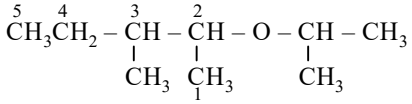
(vii) 

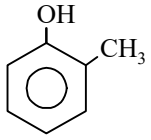
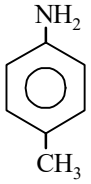
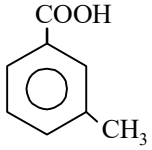
3 - (1 - Methylethyl) –2, 4 - dimethyl pent - 1 - ene

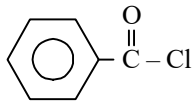
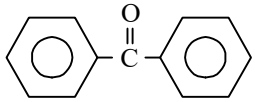
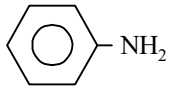
(viii) 

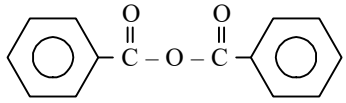
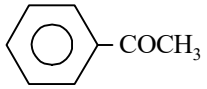
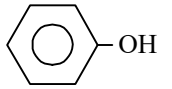
3 – N, N - Dimethyl –2, 4 - dimethyl pentan - 3 - amine

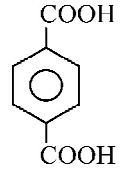
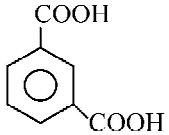
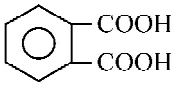
(ix)  3 - Ethyl - 2, 4, 4 - trimethyl hex - 2 - ene

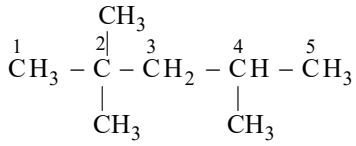
(x)  2 - (1 - Methyl ethoxy) - 3 - methyl pentane

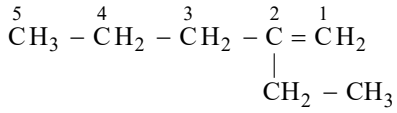
4. **(i)**  **(ii)**  **(iii)** 

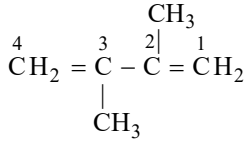
(iv)  **(v)**  **(vi)** 

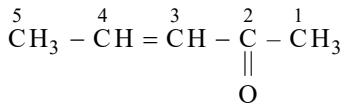
(vii)  **(viii)**  **(ix)** 

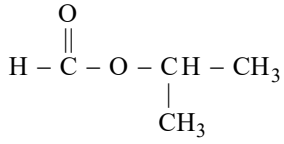
(x)  Terpthalic acid  Isophthalic acid  Phthalic acid

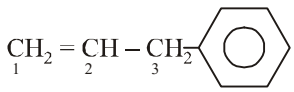
5. **(i)**  2, 2, 4 - Trimethyl pentane

(ii)  2 - Ethyl pent - 1 - ene

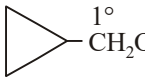
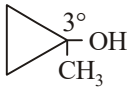
(iii)  2, 3 - Dimethyl buta –1, 3 - diene

(iv)  Pent - 3 - en - 2 - one

(v)  1 - Methyl ethyl methanoate

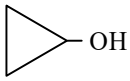
(vi)  3 - phenyl prop - 1 - ene

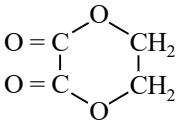
EXERCISE-B

1. **(A)** C_4H_8O :  

$CH_2 = CH - \overset{1^\circ}{CH_2} - \overset{1^\circ}{CH_2}OH$

$CH_3 - \overset{1^\circ}{CH} = CH - CH_2OH$

(B) C_3H_6O : 

(C)  ; $C_4H_4O_4$

(D) $H - \underset{\|}{C} - COOH$ (cis -) maleic acid and $H - \underset{\|}{C} - COOH$ (Trans -) fumaric acid; $C_4H_4O_4$

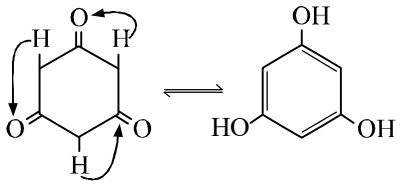
$H - \underset{\|}{C} - COOH$ $\qquad$ $HOOC - \underset{\|}{C} - H$

2. You can draw * Acids - Esters (functional isomers)

↳ among esters : Metamers

↳ among acids : chain and position (w.r.t CH_3 groups)

* hydroxy aldehydes and ketones

3. 

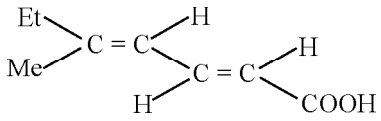
4. **(A)** $CH_3CH_2COOCH_3$; $CH_3COOC_2H_5$; $H - COO - CH_2CH_2CH_3$; $HCOO\underset{\displaystyle CH_3}{\underset{|}{C}}H - CH_3$

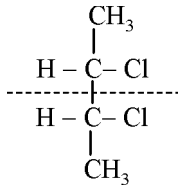
(B) $CH_3CH_2CH_2CHO$; $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}}H - CHO$

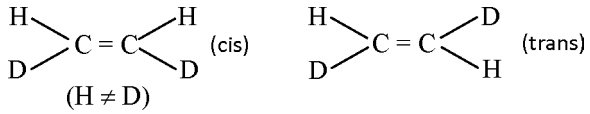
(C) $CH_3COCH_2CH_2CH_3$; $CH_3 - CO - \underset{\displaystyle CH_3}{\underset{|}{C}}H - CH_3$; $CH_3CH_2 - \overset{\displaystyle O}{\overset{\|}{C}} - CH_2 - CH_3$

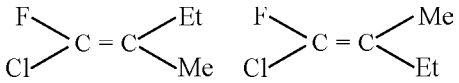
(D) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{N}} - CH_2CH_3$

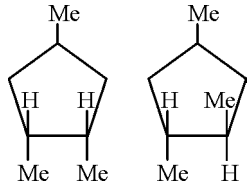
5. (B) $H_2C(Br) - CH_2 - \overset{*}{C}H(Br) - Cl$ * : chiral centre

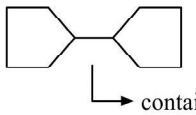
6. (D)  Observe 'two pairs of Geometric isomers ≡ 4 isomers

7. (B)  Plane of symmetry

8. (C) **II:** 

III: $F \neq Cl \neq Et \neq Me$  (In such cases cis and trans forms are not defined)

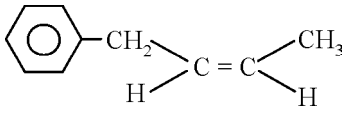
IV: 

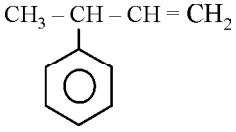
9. (C) (A) $\xrightarrow[1\text{ mole}]{H_2/Pt}$  contains 2 rings. : A must have a double bond as 1 mol of H_2 is added.

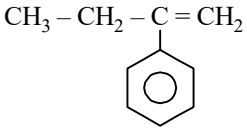
Hence, DU in A = 3

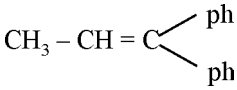
10. (C) $\overset{\uparrow}{H_2}\overset{\uparrow}{C}= \overset{\uparrow}{C}=\overset{\uparrow}{CH}-\overset{\uparrow}{CH}=O$

$sp^2 \quad sp \quad sp^2 \quad sp^2$

11. (A) **(A)** 1-phenyl-2-butene :  (shows geometric isomerism)

(B)  : Does not show geometric isomerism

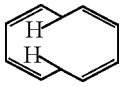
(C)  : $RCH=CH_2$ and $R_2C=CH_2$ being terminal donot show geometric isomerism.

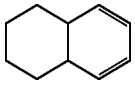
(D) 

12.(D)

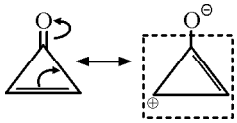
EXERCISE-C

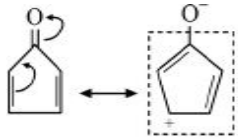
1. (AC) Ammonium ion has complete octet but carbo-cation has incomplete octet.

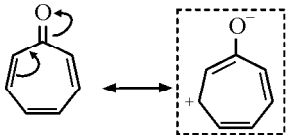
2. (D) I.  : Non aromatic due to absence of complete conjugation.

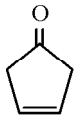
II.  : same as above

* In structures (I), the two 'H' atoms as shown exerts very high van der waal's repulsive forces causing the molecule to be non-planar.

3. (C) (I)  Aromatic (stable)

(II)  Anti-aromatic

(III)  Aromatic (stable)

(IV)  Non-aromatic (not completely conjugated however it is stable)

4.(ABD) Facts

5.(C) In (C), octet of N is being exceeded. So incorrect.

6.(B) B does not have complete conjuation and planarity.

7.(A) $CH_3 - \ddot{O}\!\!\rightarrow \overset{\oplus}{C}H_2 \longleftrightarrow CH_3 - \overset{\oplus}{O} = CH_2$ (Complete octet)

8.(B)

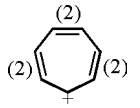
9.(D)

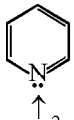
10.(AB) Check the resonance, we don't get vinylic carbocation

11.(D) All are conjugated structures.

12. (D) **(a)** $CH_2 \underset{(2)}{=} CH - CH \underset{(2)}{=} CH - \overset{-(2)}{\underset{\uparrow}{C}}H_2$: Total π e$^-$s = 6 (conjugated)

sp^2

(b)  Total π e$^-$s (conjugated) = 6

(c)  Total π e$^-$s(conjugated) = 6

$\uparrow$ sp^2 hybridised 'N' but lone pair is not conjugated.

13. (C) $\overset{\curvearrowleft}{CH_2} = CH - \overset{\curvearrowleft}{\ddot{Cl}}: \longleftrightarrow \bar{C}H_2 - CH = \overset{+}{Cl}$

$\left[\overset{\delta-}{CH_2} \cdots CH \cdots \overset{\delta+}{Cl}\right]$

$\downarrow$

x = bond length b/w C – Cl and C = Cl

$CH_3 - CH_2 - Cl$ [bond length : C – Cl] $\Rightarrow$ y > x
(y)

14. (B) I is most stable as all the atoms have complete octets with no charge separations.
II is less stable than III as in II, '+' charge is over more electronegative elements ('O').

15. (B) A, D : Tautomerism. ; (B) $CH_3 - \overset{+}{C}H - \overset{\curvearrowleft}{\ddot{O}}H \longleftrightarrow CH_3 - CH = \overset{+}{\ddot{O}}H$

16. (B) II is more stable as more electronegative elements carries '–' charge.

17.(BC) In (A) and (D), No conjugation is present

EXERCISE-D

1.(B) Inductive effect order $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}->CH_3-\overset{\overset{CH_3}{|}}{CH}->CH_3-CH_2-$

2.(B) $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \xrightarrow[\text{cleavage}]{\text{homolytic}} -\overset{|}{\underset{|}{C}}_{\bullet}$ sp^2 hybridised.

3.(ABD) $(CH_3)_3\overset{\oplus}{C}$ sp^2, planar and can lose H^+ to attain stability.

4.(C) Most stable C^+ among the given will be $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{C}}}$ ($9\ \alpha$ - $H \equiv 9$ hyperconjugative structure)

5.(A) $C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3 > C_6H_5-\overset{\oplus}{C}H-CH_3 > C_6H_5-\overset{\oplus}{C}H_2 > C_6H_5-CH_2-\overset{\oplus}{C}H_2$

Resonance, 3° Resonance, 2° Resonance, 1° No Resonance

6.(B) $C_6H_5\overline{C}H_2 > CH_3-\overline{C}H_2 > CH_3-\overline{C}H-CH_3 > CH_3-\underset{\underset{CH_3}{|}}{\overline{C}}-CH_3$ (+I - effect destabilises carbanion)

Resonance 1° 2° 3°

7.(B) $C_6H_5-\overset{\circ}{C}H-CH_3$ (2° and resonance stabilised)

8.(ABD) H_2O, NH_3 and $C_2H_5NH_2$ (All have lone pairs)

9.(CD) $\overset{+}{C}H_3$ & BF_3 both are e^- deficient, so act as electrophiles. **10.(A)**

11.(D) $CH_2=CH-\overset{\oplus}{C}H_2$ (all are sp^2 hybridised).

12.(A) $C_6H_5-\overset{+}{C}H-CH_3$ ($ph\overset{+}{C}HCH_3 > Me_3C^+ > H_2C=CHCH_2^+ >> \overset{+}{C}H_3$)

(Resonance, 2°)

13.(ABC) Definition **14.(ABCD)** Definition **15.(B)** By definition

16.(B) $(CH_3)_4\overset{\oplus}{N}$ → No lone pair ∴ Neither electrophile nor nucleophile

→ No orbital available to accept e^-

17.(A) $CH_3-CH_2-\boxed{C=C} > (CH_3)_2CH-\boxed{C=C} > CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\boxed{C=C}$

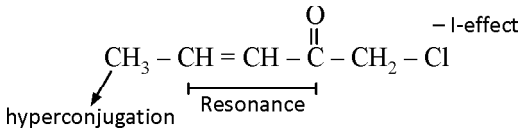
2α - Hydrogen 1 α – H 0 α – H

18.(A) C – D bond is stronger than C – H bond, so less hyperconjugation

19.(B) Check for number of α - Hydrogens for each carbocation.
(II) > (IV) > (III) > (I)
7α 4α 3α 1α

20.(ABCD) A : Methyl shift ; B,C & D : H^- shift

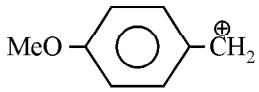
21.(C)



22.(A) Check for α - hydrogen
(II) > (IV) > (III) > (I)
12α 9α 6α 6α

23.(D) Option [3] shifts via Me-shift ; Rest undergo H^--shift.

24.(D)



MeO : Strong + M effect at p-position stabilises benzyl carbocation.

25. (B) Groups exerting –I and – M effect will stabilised carbanion.
$-NO_2$: – M, –I ; – Cl : +M, –I ; CH_3 : +M (hyper conjugation), +I

EXERCISE-E

1.(C) $$\% \ S = \frac{32 \times W_{sulphur}}{233 \times W_{BaSO_4}} \times 100$$

$$\% \ S = \frac{32 \times 0.2595}{233 \times 0.35} \times 100 = 18 \cdot 52\%$$

2.(B) Organic compound having carbon, nitrogen & sulphur form NaSCN during preparation of soda extract in Lassaigne test. NaSCN reacts with ferric chloride to form blood red coloured ferric thiocyanide.

$$3NaSCN + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric thiocynide}\\ \text{(Blood red colour)}}}{Fe(SCN)_3} + 3NaCl$$

3.(C) Mass of silver salt = 0.228g
Mass of silver = 0.162g

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of silver}} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

$$\text{Eq. of silver salt} = \frac{0.228}{0.162} \times 108$$

$$E + 107 = \frac{0.228}{0.162} \times 108$$

$$E = \left[\frac{0.228}{0.162} \times 108 - 107\right] = 45$$

Mol mass of acid = Eq. mass × basicity
$= 45 \times 2 = 90$

4.(ABD) Kjeldahl method is not suitable for those organic compound which give off N_2 on heating.

Urea : $NH_2CONH_2 \xrightarrow{\Delta} N_2 + CO + 2H_2$

5.(BC) Organic compound having carbon, nitrogen & sulphur form NaSCN during preparation of soda extract in Lassaigne test. NaSCN reacts with ferric chloride to form blood red colour ferric thiocyanide.

$$3NaSCN + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric thiocynide}\\ \text{(Blood red colour)}}}{Fe(SCN)_3} + 3NaCl$$

6.(C) Because of absence of carbon in hydrazine it can not form NaCN.

7.(B) For the test of halogen it is necessary to remove sodium cyanide and sodium sulphide from the sodium extract if nitrogen and sulphur are present. This is done by the boiling of sodium extract with concentrated nitric acid.

8.(A) Let volume of unreacted 0.1 M (= 0.2 N) H_2SO_4 be V ml.

$\therefore$ 20 ml of 0.5 M NaOH $\equiv$ V ml of 0.2 N H_2SO_4

$\therefore$ $20 \times 0.5 = V \times 0.2$

$\therefore$ $V = 50$ ml

Volume of used $H_2SO_4 = (100 - 50)$ ml

$$\% \text{ of Nitrogen} = \frac{1.4NV}{W} \quad (\text{Where N is Normality of } H_2SO_4, \text{ V is Volume of } H_2SO_4 \text{ used})$$

$$\% \text{ of Nitrogen} = \frac{1.4 \times 0.2 \times 50}{0.30} = 46.67\%$$

% Nitrogen in

(A) $NH_2CONH_2 = \frac{28 \times 100}{60} = 46.67\%$

(B) $NH_2CSNH_2 = \frac{28 \times 100}{76} = 36.84\%$

(C) $CH_3CONH_2 = \frac{14 \times 100}{59} = 23.73\%$

(D) $C_6H_5CONH_2 = \frac{14 \times 100}{122} = 23.73\%$

Hence organic compound is urea.

9.(A) $3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow \underset{\substack{\text{Ferri-ferrocynide}\\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$

10.(A) $\%p = \frac{62 \times W_{Mg_2P_2O_7}}{222 \times W_{\text{organic comp}}} \times 100 = \frac{62 \times 0.222}{222 \times 0.10} \times 100 = 62\%$

11.(C) Equivalent of Ag = Equivalent of silver salt of monobasic acid

$$\frac{60}{108} = \frac{100}{E_{\text{silver salt}}} \qquad \text{(mass of silver salt of monobasic acid is 100 gram)}$$

$$E_{\text{monobasic organic acid}} = E_{\text{silver salt of monobasic organic acid}} - E_{Ag} + E_H$$

$$= 180 - 108 + 1 = 73$$