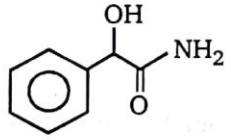
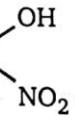
11 CARBENE AND NITRENE

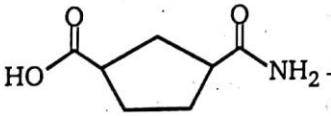
LEVEL-1

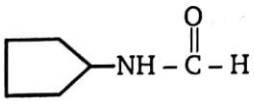
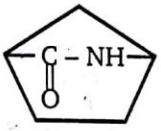
1.  $\xrightarrow{Br_2/KOH}$ product;

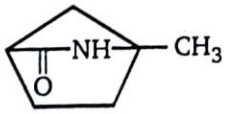
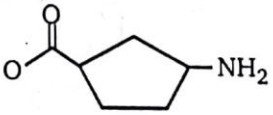
(α-hydroxy amide)

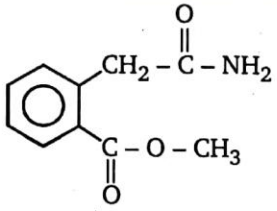
Product of this Hoffmann bromamide reaction is :

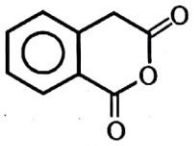
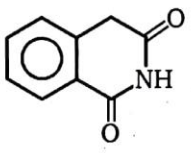
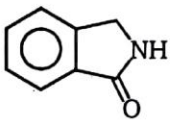
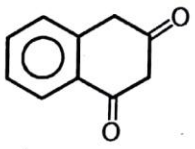
(a) $Ph-\overset{\overset{O}{\|}}{C}-CH_3$ (b) $Ph-CHO$ (c)  (d) $Ph-CH_2-NH_2$

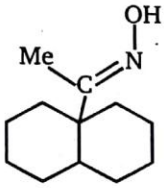
2.  $\xrightarrow{KOBr}$ $(A)\xrightarrow[\Delta]{}(B)$. Compound (B) is :

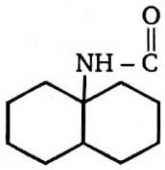
(a)  (b) 

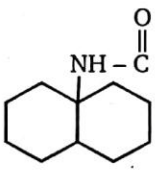
(c)  (d) 

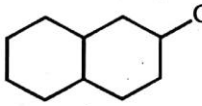
3.  $\xrightarrow{KOBr}$ (*A*); Product (*A*) is :

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

4.  $\xrightarrow{H_2SO_4}$ Product and name of the reaction is :

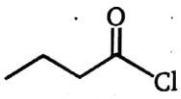
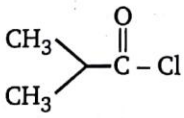
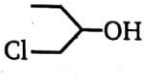
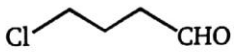
(a)  (Hoffmann bromamide reaction)

(b)  (Beckmann rearrangement)

(c)  (Curtius reaction)

(d) None of these

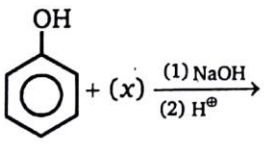
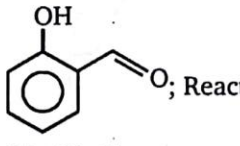
5. $(X)C_4H_7OCl \xrightarrow{NH_3} C_4H_9ON \xrightarrow[KOH]{Br_2} CH_3CH_2CH_2NH_2$; Compound (*X*) is :

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

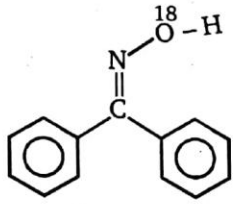
6. Which of the following will not give Hoffmann bromamide reaction ?

(a) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ (b) $Ph-\overset{O}{\overset{\|}{C}}-NH_2$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-NH-Br$ (d) $Ph-\overset{O}{\overset{\|}{C}}-NH-Ph$

7.  $\xrightarrow[(2)\ H^{\oplus}]{(1)\ NaOH}$  ; Reactant *x* is :

(a) CH_3Cl (b) CH_2Cl_2 (c) $CHCl_3$ (d) CCl_4

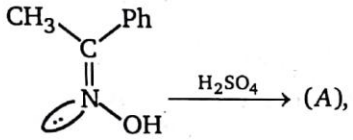
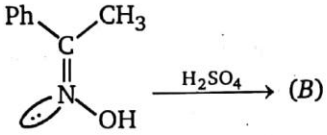
8.  $\xrightarrow[H_2O^{18}]{H_2SO_4}$ (*A*). Product (*A*) of the reaction is :

(a) $Ph-NH-\overset{\overset{O}{\|}}{C}-Ph$

(b) $Ph-NH-\overset{\overset{O^{18}}{\|}}{C}-Ph$

(c) $(Ph)_2-\overset{\overset{OH}{|}}{C}-NH_2$

(d) $Ph-CH_2-NH-Ph$

9.  $\xrightarrow{H_2SO_4}$ (*A*),  $\xrightarrow{H_2SO_4}$ (*B*)

Product (*A*) & (*B*) respectively in the above reaction are :

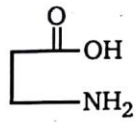
(a) $Ph-\overset{\overset{O}{\|}}{C}-NH-CH_3$, $Ph-\overset{\overset{O}{\|}}{C}-NH-CH_3$

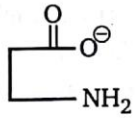
(b) $CH_3-\overset{\overset{O}{\|}}{C}-NH-Ph$, $CH_3-\overset{\overset{O}{\|}}{C}-NH-Ph$

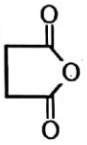
(c) $Ph-\overset{\overset{O}{\|}}{C}-NH-CH_3$, $CH_3-\overset{\overset{O}{\|}}{C}-NH-Ph$

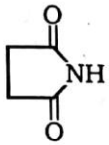
(d) $CH_3-\overset{\overset{O}{\|}}{C}-NH-Ph$, $Ph-\overset{\overset{O}{\|}}{C}-NH-CH_3$

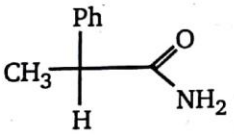
10. NBS $\xrightarrow{KOBr}$ (*A*) . Product (*A*) is :

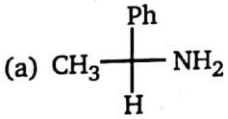
(a) 

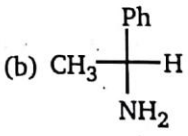
(b) 

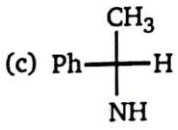
(c) 

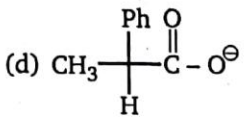
(d) 

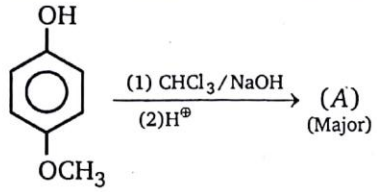
11.  $\xrightarrow[\text{(major)}]{NaOBr}$ (*A*) ; Product of the reaction is :

(a) 

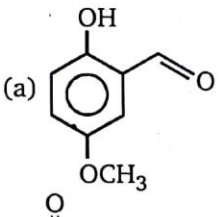
(b) 

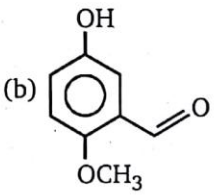
(c) 

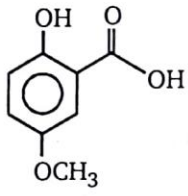
(d) 

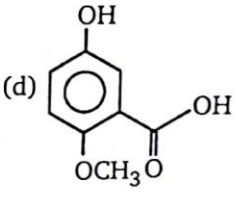
12. 

Product (*A*) is :

(a) 

(b) 

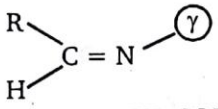
(c) 

(d) 

13. $R-\overset{O}{\overset{\|}{C}}-NH_2 + x NaOH + Br_2 \longrightarrow R-NH_2 + 2NaBr + Na_2CO_3 + H_2O$

Number of moles of NaOH used in above Hoffmann bromamide reaction is :

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

14. 

, Rate of reaction toward Beckmann rearrangement

when $\gamma = \underset{(i)}{CH_3CO_2^-}, \quad \underset{(ii)}{Cl-CH_2-CO_2^-}, \quad \underset{(iii)}{Ph-SO_3^-}$

(a) (i) > (ii) > (iii) (b) (ii) > (i) > (iii)

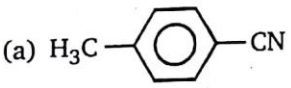
(c) (iii) > (ii) > (i) (d) (iii) > (i) > (ii)

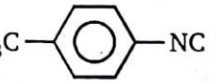
15. When primary amine reacts with chloroform in ethanolic KOH, then product is :

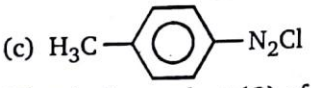
(a) an isocyanide (b) an aldehyde

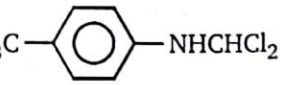
(c) a cyanide (d) an alcohol

16. The reaction of chloroform with alcoholic KOH and *p*-toluidine forms :

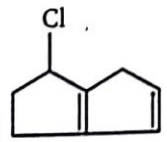
(a) 

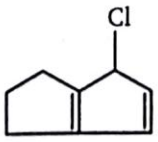
(b) 

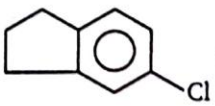
(c) 

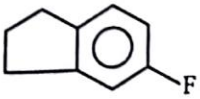
(d) 

17. What is the product (*Q*) of the following reaction ?

(a) 

(b) 

(c) 

(d) 

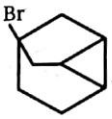
18. 

$\xrightarrow[\Delta]{\text{NaOH, 50\%}}$ (*A*) ; Product (*A*) is :

(a) 

(b) 

(c) 

(d) 

19. Which of the following reaction, does not give chloro benzene as a product ?

(a)  $\xrightarrow{CHCl_3,\ HO^-}$

(b)  $\xrightarrow{CHBrCl_2,\ HO^-}$

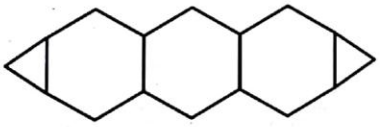
(c)  $\xrightarrow{CHBr_2Cl,\ HO^-}$

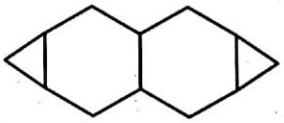
(d)  $\xrightarrow{CHFClBr,\ HO^-}$

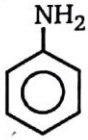
20. 
$\xrightarrow[Zn/Cu]{\text{(3 mole) } CH_2I_2}$ (*A*) ; Compound (*A*) is :

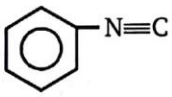
(a) 

(b) 

(c) 

(d) 

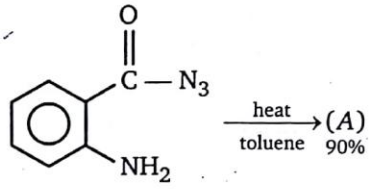
21. 

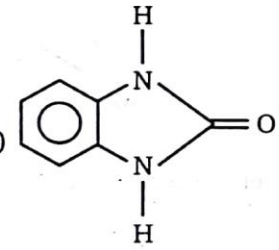
$+ CHCl_3 + xKOH \longrightarrow$ 

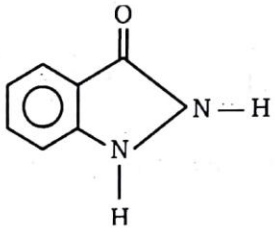
x = moles of KOH consumed is :

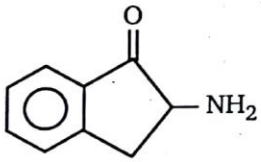
(a) 1 (b) 2 (c) 3 (d) 4

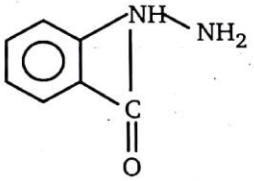
22. Heating the acyl azide in dry toluene under reflux for 3-hours give a 90% yield for a heterocyclic product. Identify the product (*A*).

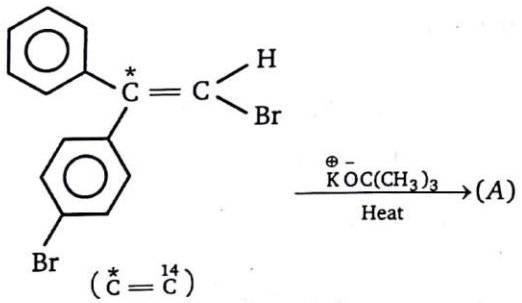

O
C — N3
NH2
heat
toluene
(A)
90%

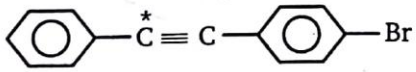
(a) 
H
N
O
N
H

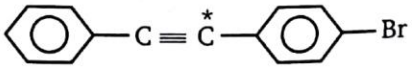
(b) 
O
N — H
N
H

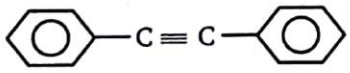
(c) 
O
NH2

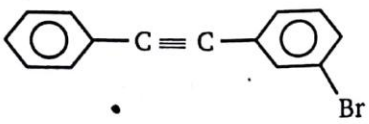
(d) 
NH
NH2
C
O

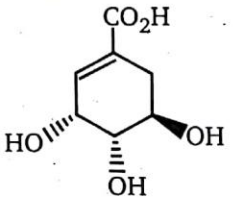
23. 
H
Br
Br
Heat
(A)

(a) 
C ≡ C
Br

(b) 
C ≡ C
Br

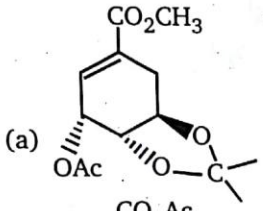
(c) 
C ≡ C

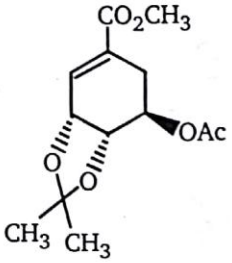
(d) 
C ≡ C
Br

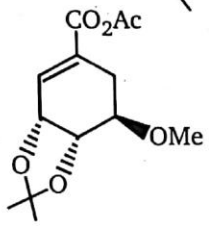
24. 

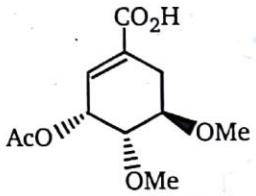
$\xrightarrow[\text{(2) acetone/H}^+\text{(3)Ac}_2\text{O, Acetic anhydride}]{\text{(1) CH}_2\text{N}_2}$ (*A*) (de-colourises Br_2 water)

Product (*A*) of the above reaction is :

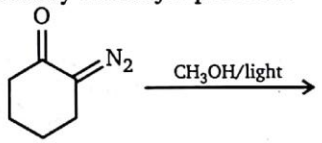
(a) 

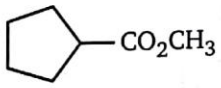
(b) 

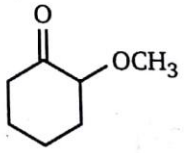
(c) 

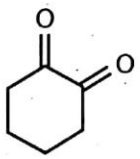
(d) 

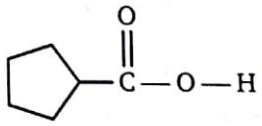
25. A rather interesting example of the Wolff rearrangement with 2-diazocyclohexanone in methanol is given below. Identify the major product :



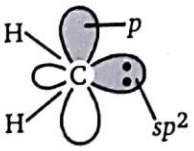
(a) 

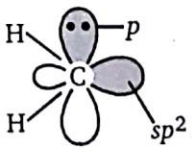
(b) 

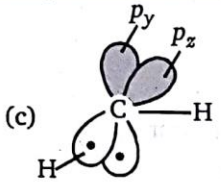
(c) 

(d) 

26. The orbital picture of a singlet carbene ($:CH_2$) can be drawn as :

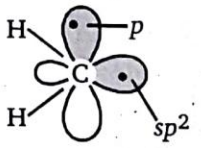
(a) 

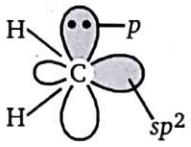
(b) 

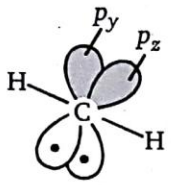
(c) 

(d) none of these

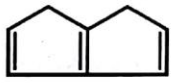
27. The orbital picture of a triplet carbene can be drawn as :

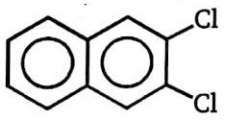
(a) 

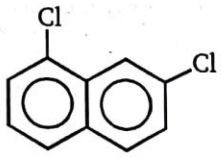
(b) 

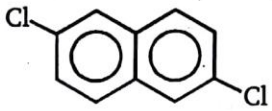
(c) 

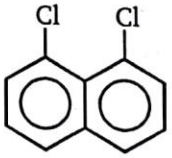
(d) none of these

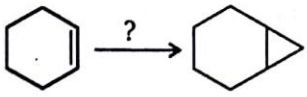
28.  $\xrightarrow[KOH]{CHCl_3}(A)\xrightarrow[KOH]{CHCl_3}(B)$; Product (B) is :

(a) 

(b) 

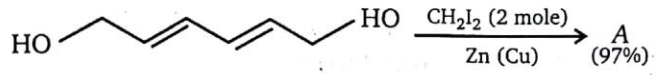
(c) 

(d) 

29. 

Select the suitable reagent for above conversion.

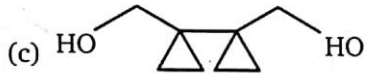
(a) CH_2N_2 / Δ
(b) CBr_4 / RLi
(c) $H_2C=CH_2$
(d) t-BuOK

30. 

Product (*A*) will be :

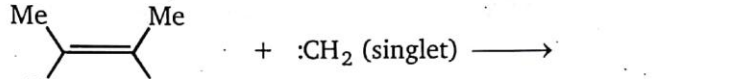
(a) 

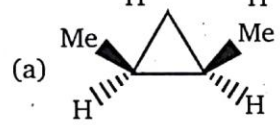
(b) 

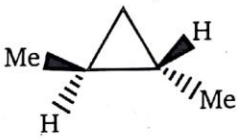
(c) 

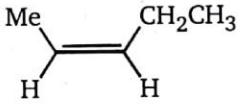
(d) 

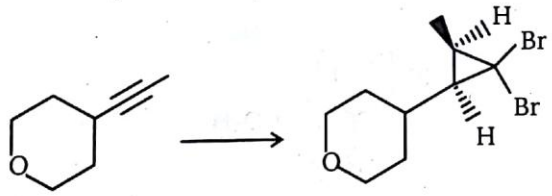
31. The major product formed in the following reaction is



(a) 

(b) 

(c) 50 : 50 mixture of above two compounds (d) 

32. 

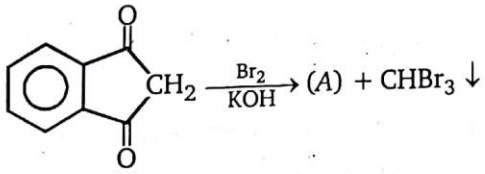
To carry out above conversion reagent used in decreasing order.

(a) $Na/liq.\ NH_3$, $CHBr_3/NaOH(\Delta)$

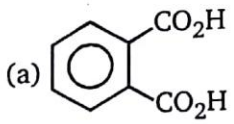
(b) $H_2/Pd - CaCO_3, CHBr_3/NaOH(\Delta)$

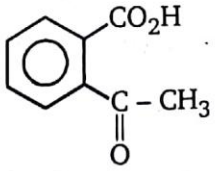
(c) $Na/liq.\ NH_3$, $CHCl_3/NaOH$

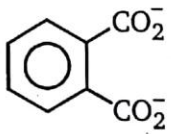
(d) $H_2/Pd - CaCO_3, CHCl_3/NaOH$

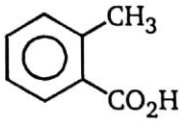
33. 

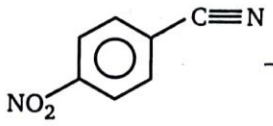
Product (*A*) of the reaction is :

(a) 

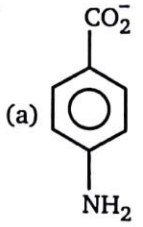
(b) 

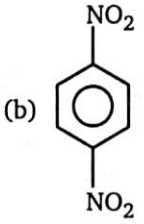
(c) 

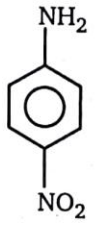
(d) 

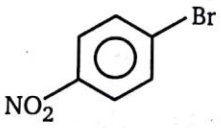
34. 

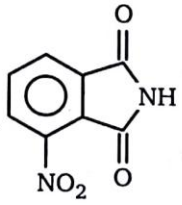
$\xrightarrow[(2)\ HO^-, Br_2]{(1)\ HO^-(1\ mole)}$ (*A*); Product (*A*) is :

(a) 

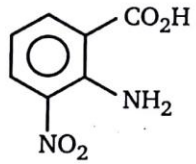
(b) 

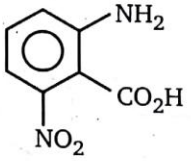
(c) 

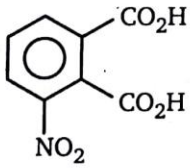
(d) 

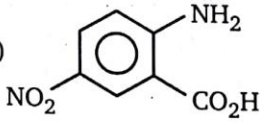
35. 

$\xrightarrow[H_2O]{NaOCl}$ (*X*) ; Product *X* will be :
(80%)

(a) 

(b) 

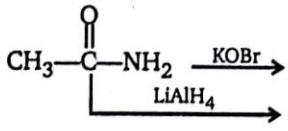
(c) 

(d) 

36. $CH_3-CH_2-CH_2-CH_2-CH_3 \xrightarrow{CH_2N_2/\Delta}$ Products

Which of the following product(s) is/are can be obtained in the above reaction.

(a) Isopentane (b) 3-Methyl hexane (c) *n*-Pentane (d) 3-Methyl pentane

37. 

Relation between (*A*) & (*B*) is :

(a) Identical (b) Functional isomer (c) Homologous (d) Positional isomers

38. If we use pyrene (CCl_4) in the Riemer-Tiemann reaction in place of chloroform, the product formed is :

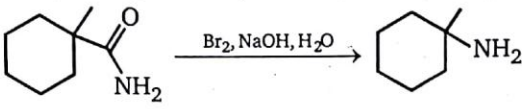
(a) Salicylaldehyde (b) Phenolphthalein (c) Salicylic acid (d) Cyclohexanol

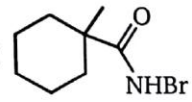
39. When ethyl amine is heated with chloroform and alcoholic KOH, a compound with offensive smell is obtained. This compound is :

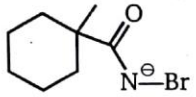
(a) A secondary amine (b) An isocyanide

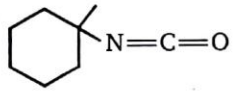
(c) A cyanide (d) An acid

40. Which of the following species would not be involved in the Hoffmann rearrangement shown below ?



(a) 

(b) 

(c) 

(d) All of the above are involved in the reaction.

41. In which of the following reactions migration of alkyl group from carbon to oxygen is observed ?

(a) Pinacol-pinacolone rearrangement

(b) Bayer-villiger oxidation.

(c) Prepration of phenol from cumene hydroperoxide.

(d) Both (b) & (c)

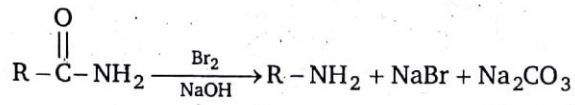
ANSWERS — LEVEL 1

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

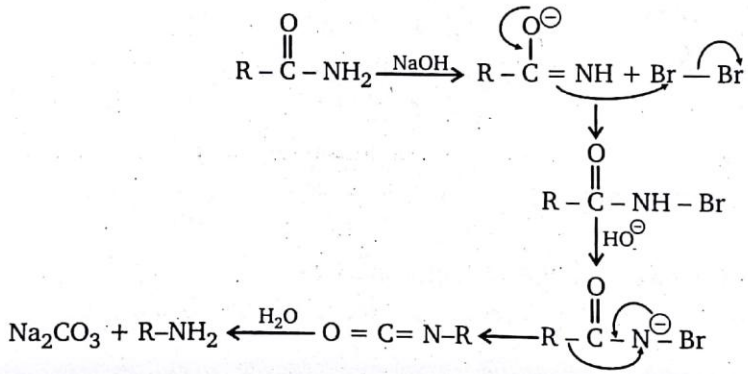
LEVEL-2

1. Comprehension

Hoffmann bromamide reaction involves conversion of a carboxylic acid amide into an amine with a loss of a carbon atom on treatment with aqueous sodium hypobromite. Thus Hoffmann result in shortening of a carbon chain.

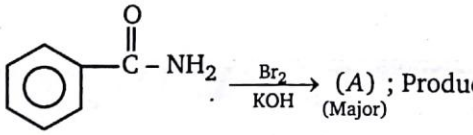


Mechanism of the reaction is :



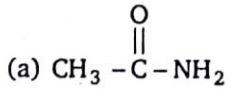
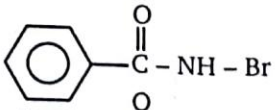
A. Number of moles of NaOH consumed in above reaction.

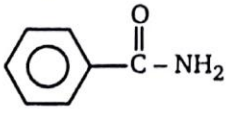
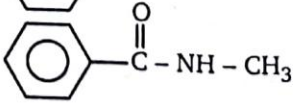
(a) 1 (b) 2 (c) 3 (d) 4

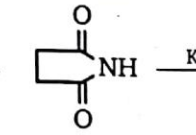
B.  ; Product (*A*) :

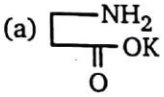
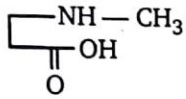
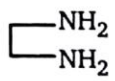
(a) $Ph-NH_2$ (b) $Ph-CH_2-NH_2$ (c) $Ph-NH-CH_3$ (d) 

C. Which of the following will not give Hoffmann bromamide reaction.

(a)  (b) 

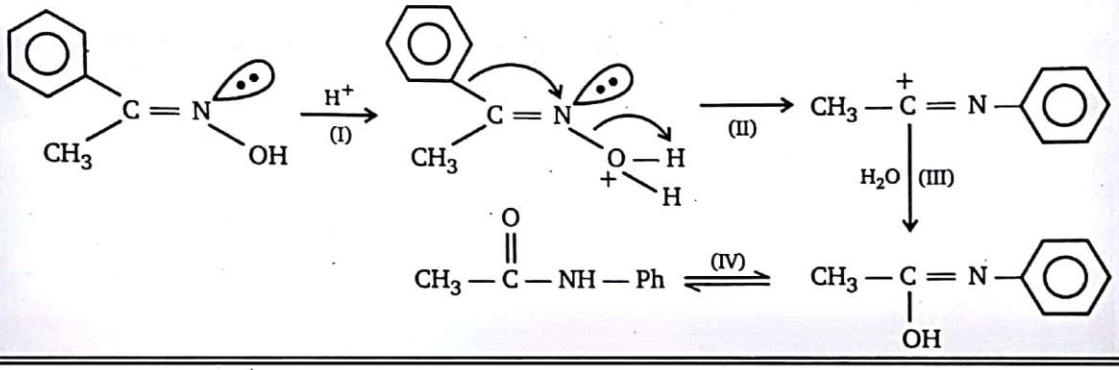
(c)  (d) 

D.  $\xrightarrow{KOBr}$ (*A*), Product (*A*) is :

(a)  (b)  (c)  (d) None of these

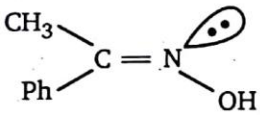
2. Comprehension

Given is mechanism of Beckmann rearrangement.



A. Rate determining step in Beckmann rearrangement :

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

B. 

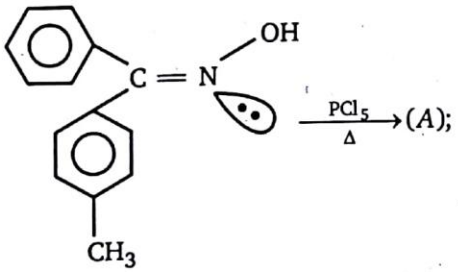
On treatment H_2SO_4 followed by hydrolysis in acidic medium above compound gives.

(a) CH_3-CO_2H, $Ph-NH_2$ (b) CH_3-NH_2, $Ph-CO_2H$

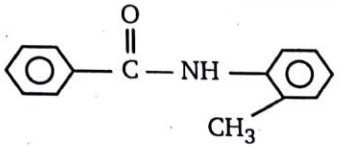
(c) $Ph-CH_2-NH_2+Ph-CO_2H$ (d) $Ph-CO_2H+CH_3-CO_2H$

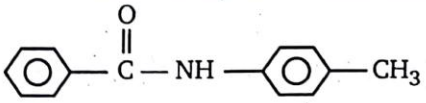
C. Which of the following reagent cannot used in Beckmann rearrangement ?

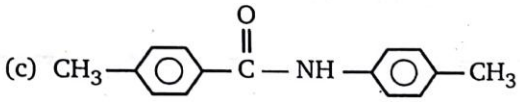
(a) TsOH (b) $R-SO_2Cl$ (c) BF_3 (d) $Ph-Li$

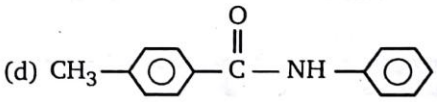
D. 

Product (*A*) of the above reaction is :

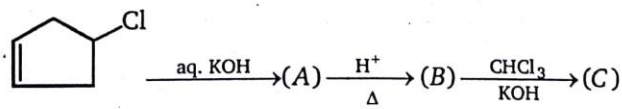
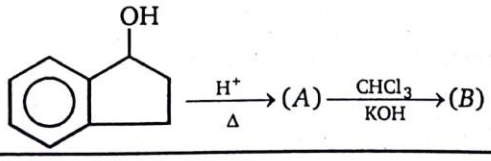
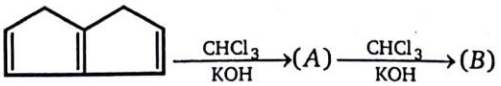
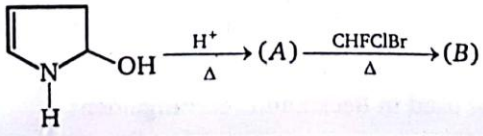
(a) 

(b) 

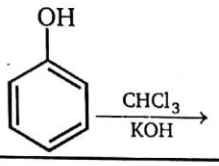
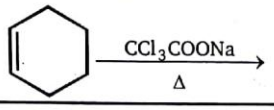
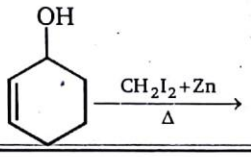
(c) 

(d) 

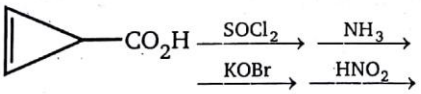
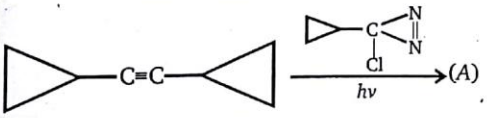
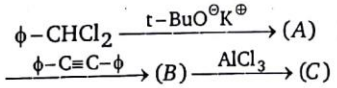
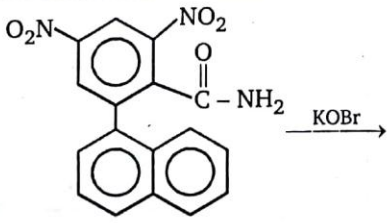
3. Match the column I and II.

	Column (I)		Column (II)
(a)		**(p)**	D.B.E. = even for product (Double bond equivalent)
(b)		**(q)**	D.B.E. = odd for product
(c)		**(r)**	Ring expansion takes place
(d)		**(s)**	Carbene will formed

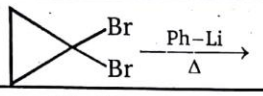
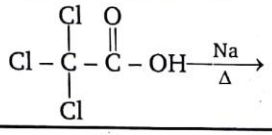
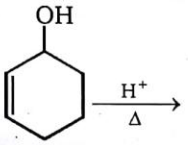
4. Match the column I and II.

	Column (I)		Column (II)
(a)		**(p)**	Reimer Tiemann reaction
(b)		**(q)**	Reimer Tiemann expansion (**or**) Abnormal RNT reaction
(c)		**(r)**	Simman-smith reaction.
(d)		**(s)**	Increase in carbon takes place

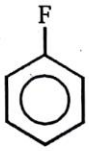
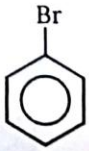
5. Match the column I and II.

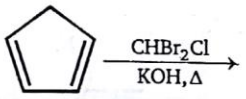
	Column (I)		Column (II)
(a)		**(p)**	Aromatic compound will formed
(b)		**(q)**	Migration take place from carbon to electron deficient nitrogen
(c)		**(r)**	Carbene will formed in this reaction
(d)		**(s)**	N_2 will evolve.

6. Match the column I and II:

Column (I)		Column (II)	
Reaction		**Intermediate**	
(a)	$CHCl_3 + KOH \xrightarrow[\Delta]{}$	**(p)**	Carbocation
(b)		**(q)**	Carbanion
(c)		**(r)**	Free radical
(d)		**(s)**	Carbene

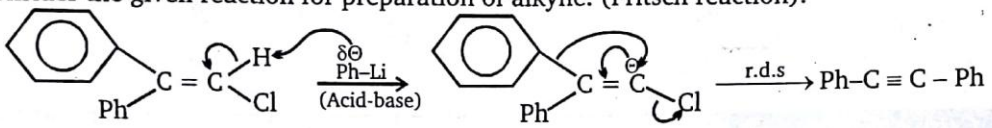
7. Matrix :

Column (I)		Column (II)	
Reaction		**Product**	
(a)		**(p)**	
(b)		**(q)**	
(c)		**(r)**	

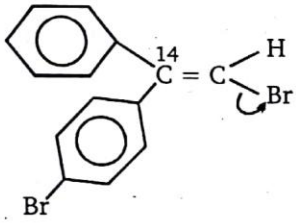
(d)		(s)	

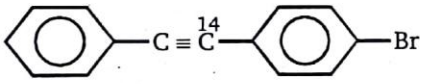
8. Comprehension

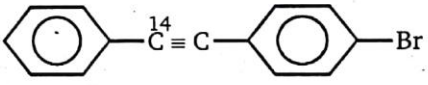
1. Consider the given reaction for preparation of alkyne. (Fritsch reaction).



Anti group will migrate because of less steric hindrance.

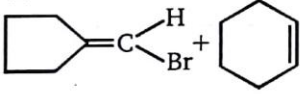
A.  $\xrightarrow[\Delta]{\overset{\oplus}{K}\overset{\ominus}{O}C(CH_3)_3}$ (*A*) ; Major product (*A*) is :
(major)

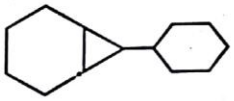
(a) 

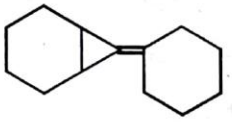
(b) 

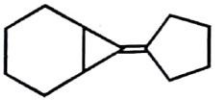
(c) $Ph - C \equiv C^{14} - Ph$

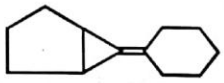
(d) $Ph - C \equiv C - Ph$

B.  $+ K^{\oplus}O^{\ominus}C(CH_3)_3 \xrightarrow[\Delta]{} (A)$, product (*A*) is :

(a) 

(b) 

(c) 

(d) 

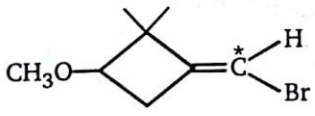
C. Rate of reaction when the halide ion:

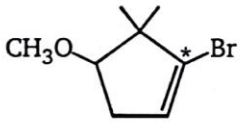
(a) $I^{\ominus} > Cl^{\ominus} > Br^{\ominus} > F^{\ominus}$

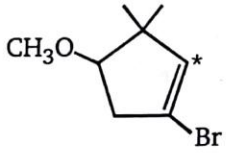
(b) $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

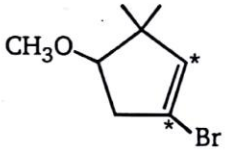
(c) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

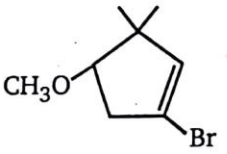
(d) $F^{\ominus} > Br^{\ominus} > Cl^{\ominus} > I^{\ominus}$

D.  $\xrightarrow[\Delta]{t\text{-BuOK}}$ (*A*) (Major) , Product (*A*) is : ($C^* = C^{14}$)

(a) 

(b) 

(c) 

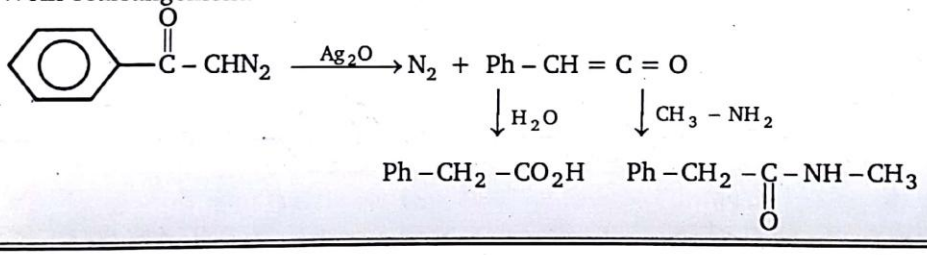
(d) 

9. Comprehension

Wolff rearrangement

When α-Diazoketones are photo-irradiated or heated at high temperature or reacted with silver oxide or silver salts at room temperature, they loose nitrogen and rearrange to form ketene.

The ketenes reacts rapidly with water, alcohol and amines. Therefore, the reactions called Wolff-rearrangement.



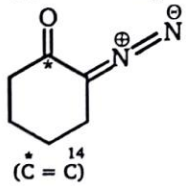
A. $Ph-\overset{\overset{O}{\|}}{\underset{14}{C}}-CHN_2 \xrightarrow[H_2O]{Ag_2O} (A)$, Product (A) is :

(a) $Ph-\overset{14}{C}H_2-CO_2H$

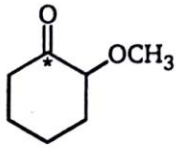
(b) $Ph-CH_2-\overset{14}{C}O_2H$

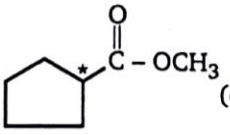
(c) $Ph-\overset{14}{C}O_2H$

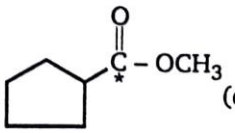
(d) $Ph-CO_2H$

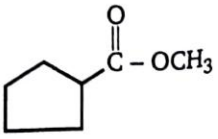
B. 

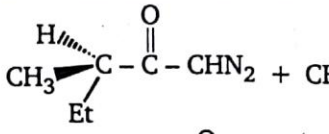
$\xrightarrow[h\nu]{CH_3OH}$ (A) (Major), Product (A) is :

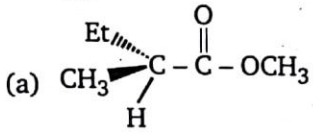
(a) 

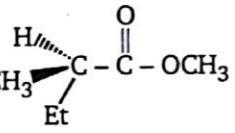
(b) 

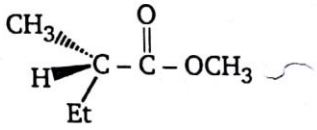
(c) 

(d) 

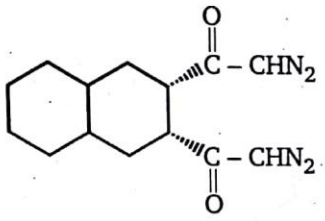
C.  $\xrightarrow{Ag_2O}$ Major product of the reaction is :

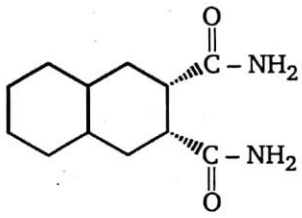
(a) 

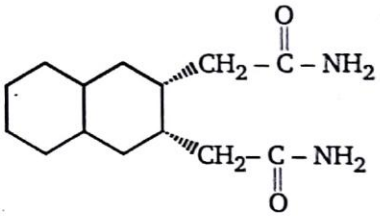
(b) 

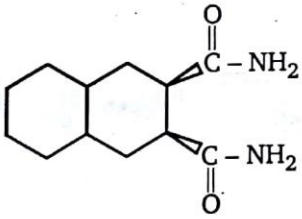
(c) 

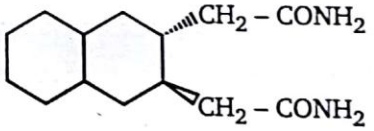
(d) None of these

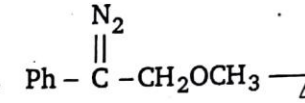
D.  $\xrightarrow[NH_3]{Ag_2O}$ (*A*) (Major) , Product (*A*) is :

(a) 

(b) 

(c) 

(d) 

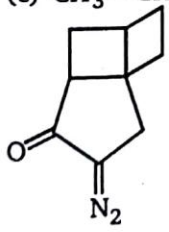
E.  $\xrightarrow[\Delta]{}$ (*A*) 90% , product (*A*) is :

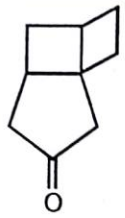
(a) $Ph - CH = CH - OH$

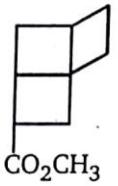
(b) $Ph - CH = CH - OCH_3$

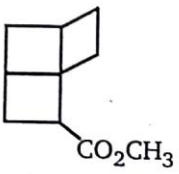
(c) $CH_3 - CH = CH - O - PH$

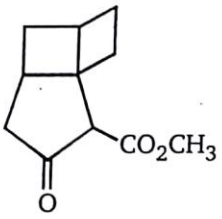
(d) $CH_3 - CH = CH - OH$

F.  $\xrightarrow[CH_3OH]{h\nu}$ (*A*) , Product (*A*) is :

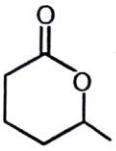
(a) 

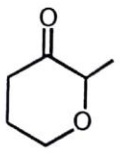
(b) 

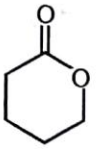
(c) 

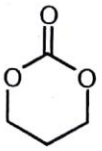
(d) 

G. $HO-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CHN_2 \xrightarrow[\Delta]{Ag_2O} (A)$, Product (*A*) is :

(a) 

(b) 

(c) 

(d) 

ANSWERS — LEVEL 2

1. A – d, ; B – a; C – d, ; D – a,

2. A – b; B – b; C – d; D – b

3. a – p, r, s; b – q, r, s; c – q, r, s; d – p, r, s

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

5. a – p, q, s; b → p, r, s ; c – p, r ; d – p, q

6. a – q, s; b – q, s; c – q, s; d – p

7. a – q; b – p; c – q; d – q

8. A – a; B – c; C – b; D – b

9. A – b; B – c; C – d; D – b; E – b; F – b; G – c