



CHEMISTRY

BOOKS - MS CHOUHAN

CARBENE AND NITRENE



1. 📄

Product of this Hoffmann bromamide reaction is :

A.
$$Ph - \overset{O}{\overset{||}{C}} - CH_3$$

$$\mathsf{B}. Ph-CHO$$

C. 📄

D. $Ph - CH_2 - NH_2$



Answer: B





Product (A)

is :







C.

Β.



Answer: C





4.

Product and name of the reactions is :







D. None of these

Answer: B



5.
$$(A) \stackrel{NH_3}{\longrightarrow} (B) \stackrel{KOH \, / \, Br_2}{\longrightarrow} (CH_3)_2 CHNH_2$$
 A is





Β.







Answer: A



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. $Ph - \overset{O}{\overset{||}{C}} - NH - Ph$

Answer: D



is :

A. CH_3Cl

 $\mathsf{B.}\, CH_2 Cl_2$

 $C. CHCl_3$

D. CCl_4

Answer: C



Product (A)

of the reaction is:

8.

A.
$$Ph - NH - \overset{O}{\overset{||}{C}} - Ph$$

B. $Ph - NH - \overset{O^{18}}{\overset{||}{C}} - Ph$
 $\overset{OH}{\overset{OH}{C}}$
C. $(Ph)_2 - \overset{|}{\overset{OH}{C}} - NH_2$

D.
$$Ph - CH_2 - NH - Ph$$

Answer: B



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

Answer: C

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









Answer: B

C.



the reaction is :







C.



Answer: A





Product (A) is:





Β.

C.





Answer: A

D.



13.

$$\stackrel{O}{\stackrel{||}{R}}_{R-C} - NH_2 + xNaOH + Br_2
ightarrow R - NH_2 + 2NaBr + Na_2CO_3 + H$$

Number of moles of NaOH used in above Hoffmann bromamide reaction

is :

A. 3

B. 4

C. 5

D. 6

Answer: B



reaction toward Backmann rearrangement

when $\gamma = CH_3CO_2^-$, $Cl - CH_2 - CO_2^-$, $Ph - SO_3^-$

A.
$$(i) > (ii) > (iii)$$

$$\mathsf{B}.\,(ii)>(i)>(iii)$$

$$\mathsf{C}.\left(iii
ight)>\left(ii
ight)>\left(i
ight)$$

Answer: C

14.

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15. A primary amine on reaction with alc. KOH and chloroform yields

A. an isocyanide

B. an aldehyde

C. a cyanide

D. an alcohol

Answer: A

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16. The reaction of chioroform with alcoholic KOH and p-toludine forms











Answer: D





18.

, Product

(A) is :



A.



Β.





D.

C.

Answer: A



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



Answer: D

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$$(3 \text{ mole}) CH_2 l_2 \rightarrow (A)$$

$$Zn/Cu$$

20.

Compound (A) is :



A.



Β.



Answer: A



 NH_2 - N==C + CHCl₃ + xKOH -21.

x = moles of KOH consumed is :

A. 1 B. 2

D. 4

C. 3

Answer: C

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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).







Β.

A.





Answer: A

D.

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23.









Answer: B





24.

(de-colourises Br_2 water)

Product (A) of the above reaction is :









Answer: B



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









Answer: A

C.

26. The correct representation of single carbene is





Β.

A.



D. none of these

Answer: A

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





Β.

A.



D. none of these

Answer: C



(B) is:









Answer: C



Select the suitable reagent for above conversion.

A. CH_2N_2 / Δ

- B. CBr_4/RLi
- $\mathsf{C}.\,H_2C=CH_2$

D. t-BuOK

Answer: A





Answer: B



31. The major product formed in the following reaction is



C. 50:50 mixture of above two compounds



Answer: A





32.

To carry out conversion reagent used in decreasing order.

A. $Na/ ext{liq.}$ $NH_3,$ $ChBr_3/NaOH(\Delta)$

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

C. $Na/ ext{liq.}$ $NH_3,$ $CHCl_3/NaOH$

 $\mathsf{D}.\,H_2\,/\,Pd-CaCO_3,\,CHCl_3\,/\,NaOH$

Answer: B





33.

Product (A) of the reaction is :









Answer: C





(A) is :



A.



Β.




Answer: C

D.

C.

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Answer: B

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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

Answer: D

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between (A) & (B) is:

A. Identical

B. Functional isomer

C. Homologous

D. Positional isomers

Answer: C



38. If we use carbon tetrachloride in Reimer Tiemann reaction in place of

chloroform, the product formed is

A. Salicylaldehyde

B. Phenolphthalein

C. Salicylic acid

D. Cyclohexanol

Answer: C

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39. The amine which does not react with chloroform and ethanolic potassium hydroxide is

A. A secondary amine

B. An isocyanide

C. A cyanide

D. An acid

Answer: B

40. Which of the following species would not be involved in the Hoffmann

rearrangement shown below?



D. All of the above are involved in the reaction.

Answer: D



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)

Answer: D

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Level 2 Comprehension

1. 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.

$$\stackrel{O}{\substack{||\ R-C}}_{R-C} = NH_2 \xrightarrow[NaOH]{Br_2} R - NH_2 + NaBr + Na_2CO_3$$

Mechanism of the reaction is :

$$R - C - NH_{2} \xrightarrow{\text{NaOH}} R - C = NH + Br - Br$$

$$R - C - NH_{2} \xrightarrow{\text{NaOH}} R - C = NH + Br - Br$$

$$R - C - NH - Br$$

$$Hd^{\Theta}$$

$$R$$

Number of moles of NaOH consumed in above reaction.

A.	1
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- B. 2
- C. 3

D. 4

Answer: D

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2. 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.

$$\stackrel{O}{R-C} R - NH_2 \xrightarrow[NaOH]{Br_2} R - NH_2 + NaBr + Na_2CO_3$$

Mechanism of the reaction is :



A. $Ph - NH_2$

 $C. Ph - NH - CH_3$



Answer: A

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3. 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.

$$\stackrel{O}{R-C} = NH_2 \stackrel{Br_2}{\overset{Br_2}{\longrightarrow}} R - NH_2 + NaBr + Na_2CO_3$$

Mechanism of the reaction is :



Which of the following will not give Hoffmann bromamide reaction.



Answer: D

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4. 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.

$$\stackrel{O}{R-C} = NH_2 \xrightarrow[NaOH]{Br_2} R - NH_2 + NaBr + Na_2CO_3$$

Mechanism of the reaction is :

:



Product (A) is



C.

D. None of these

Answer: A





Rate determining step in Beckmann rearrangement:

A. I

B. II

C. III

D. IV

Answer: B





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

A.
$$CH_3-CO_2H, Ph-NH_2$$

 $\mathsf{B.}\,CH_3-NH_2,Ph-CO_2H$

 $\mathsf{C.}\, Ph-CH_2-NH_2+Ph-CO_2H$

 $\mathsf{D}.\, Ph-CO_2H+CH_3-CO_2H$

Answer: B



Which of the following reagent cannot used in Beckmann rearrangement?

A. TsOH

 $B.R - SO_2H$

 $C. BF_3$

D. Ph-Li

Answer: D

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Product (A) of the above reaction is :



Answer: B



 $\mathsf{C}. Ph - C \equiv C^{14} - Ph$

D. $Ph - C \equiv C - Ph$

Answer: A



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



Anti group will migrate because of less steric hindrance.





:





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



Anti group will migrate because of less steric hindrance.

Rate of reaction when the halide ion:

A.
$$I^{\Theta} > Cl^{\Theta} > Br^{\Theta} > F^{\Theta}$$

B. $I^{\Theta} > Br^{\Theta} > Cl^{\Theta} > F^{\Theta}$
C. $F^{\Theta} > Cl^{\Theta} > Br^{\Theta} > I^{\Theta}$

$$\mathsf{D}.\,F^{\,\Theta} > Br^{\,\Theta} > Cl^{\,\Theta} > I^{\,\Theta}$$

Answer: B



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



Anti group will migrate because of less steric hindrance.



Product (A) is : $\left(C^{\,*}\,=\,C^{14}
ight)$







Answer: B



13. 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.

$$\begin{array}{c} & \bigcirc \\ & \bigcirc \\ & \bigcirc \\ & C - CHN_2 \end{array} \xrightarrow{Ag_2O} N_2 + Ph - CH = C = O \\ & \downarrow H_2O \qquad \downarrow CH_3 - NH_2 \\ & Ph - CH_2 - CO_2H \qquad Ph - CH_2 - C - NH - CH_3 \\ \end{array}$$

$$Ph- \stackrel{||}{\displaystyle C_{14}} - CHN_2 \stackrel{Ag_2O}{\displaystyle ode H_{2O}} (A)$$
 , Product (A) is :

A.
$$Ph-\overset{14}{CH_2}-CO_2H$$

$$\mathsf{B}. Ph - CH_2 - CO_2H$$

C.
$$Ph-\overset{14}{CO_2N}$$

0

D.
$$Ph - CO_2H$$

Answer: B

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14. 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.



Product (A) is



:







Answer: C

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15. 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.

$$\begin{array}{c} & & & \\ & & & \\ & & & \\ & &$$



Major product of the reaction is :



D. None of these

Answer: D



16. Wolff rearrangement

a

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.

$$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$



, Product (A)

is :





Answer: B



17. 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.

$$\begin{array}{c} & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\$$

$$Ph - \stackrel{N_2}{\overset{||}{C}}{-} CH_2OCH_3 \overset{\longrightarrow}{\longrightarrow} (A)90~\%$$
 , product (A) is :

A. Ph - CH = CH - OH

 $B. Ph - CH = CH - OCH_3$

 $\mathsf{C}. \, CH_3 - CH = CH - O - Ph$

$$\mathsf{D}.\,CH_3-CH=CH-OH$$

Answer: B

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18. 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.



, Product (A)

is :





Β.



C.



Answer: B



19. 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.

 $HO-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CHN_2\stackrel{Ag_2O}{\overset{\Delta}{
ightarrow}}(A)$, Product (A) is :



A.





C.



D.

Answer: C

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1. Match the column I and II.

	Column (I)		Column (II)
(a)	$\qquad \qquad $	(p)	D.B.E. = even for product (Double bond equivalent)
(b)	$\bigcup_{A} \xrightarrow{H^{*}} (A) \xrightarrow{CHC_{3}} (B)$	(q)	D.B.E. = odd for product
(c)	$\underbrace{\bigcirc}_{\text{CHCl}_3} \xrightarrow{\text{CHCl}_3} (A) \xrightarrow{\text{CHCl}_3} (B)$	(r)	Ring expansion takes place
(d)	$\bigcup_{\substack{H\\ H}} OH \xrightarrow{H^{*}} (A) \xrightarrow{CHFClBr} (B)$	(s)	Carbene will formed

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2. Match the column I and II.

Lan.s.	Column (I)		Column (II)
(a)	$\overbrace{KOH}^{\text{CHCl}_3}$	(p)	Reimer Tiemann reaction
(b)	$\bigcup_{\text{CHCl}_3}^{\text{OH}}$	(q)	Reimer Tiemann expansion (or) Abnormal RNT reaction
(c)	$\qquad \qquad $	(r)	Simman-smith reaction.
(d)	$\overset{OH}{\overbrace{\qquad}}\overset{CH_2I_2+Zn}{\overbrace{\qquad}}$	(s)	Increase in carbon takes place

3. Match the column I and II.

....

Column (I)		Column (II)	
(a)	$ \begin{array}{c} & & \\ \hline \hline & & \\ \hline & & \\ \hline \hline \\ \hline \\$	(p)	Aromatic compound will formed
(b)	$ \begin{array}{ c } \hline $	(q)	Migration take place from carbon to electron deficient nitrogen
(c)	$\begin{array}{c} \phi - \operatorname{CHCl}_2 \xrightarrow{t - \operatorname{BuO}^{\Theta} K^{\oplus}} (A) \\ & \xrightarrow{\phi - C = C - \phi} (B) \xrightarrow{AlCl_3} (C) \end{array}$	(r)	Carbene will formed in this reaction
(d)		(s)	N ₂ will evolve.

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4. Match the column I and II.

	Column (I)		Column (II)
	Reaction		Intermediate
(a)	$CHCl_3 + KOH \xrightarrow{\Delta}$	(p)	Carbocation
(b)	$Br \xrightarrow{Ph-Li}_{Br} \xrightarrow{A}$	(q)	Carbanion
(c)	$\begin{array}{c} Cl & O \\ Cl - C - C - OH \xrightarrow{Na} \\ Cl \end{array}$	(r)	Free radical
(d)	$\stackrel{\text{OH}}{\longmapsto} \stackrel{H^{*}}{}$	(s)	Carbene

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5. Matrix :

	Column (I)		Column (II)
	Reaction	in the second	Product
(a)	$\overbrace{\qquad KOH, \Delta}^{CHCl_3}$	(p)	F-O
(b)	$\qquad \qquad $	(q)	G-O
(c)	$\underbrace{CHCl_2Br}_{KOH,\Delta}$	(r)	Br


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