

Important Questions On Intermediates





Important Questions on Intermediates

1. The major product(s) formed in the following reaction is (are)

2. The intermediate(s) involved in the following reaction is(are)?

MeO I₂, Ag₂O MeO

A. only I

C. I and II only

- B. only II
- D. I and III only
- 3. The major product formed in the following reaction is

A. Br

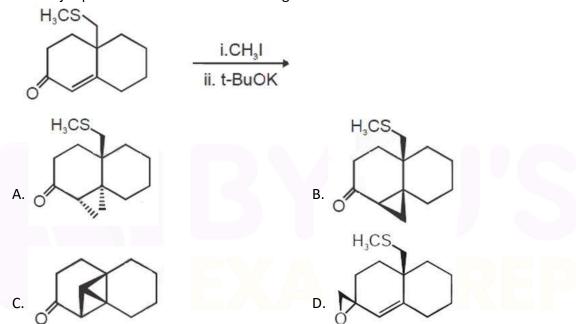
- 4. The frontier orbital interactions involved in the formation of the carbocation intermediate in the reaction of isobutylene with HCl are
 - A. π of olefin and σ^* of HCl
 - B. π of olefin and σ of HCl
 - C. π^* of olefin and σ^* of HCl
 - D. π^* of olefin and σ of HCl



5 .The correct order of the rate constants for the following series of reactions (Z = $CF_3/CH_3/OCH_3$) is

$$Z \longrightarrow Br$$
 + H-N $Z \longrightarrow NO_2$
A. $CF_3 > CH_3 > OCH_3$ B. $CF_3 > OCH_3 > CH_3$
C. $OCH_3 > CF_3 > CH_3$ D. $CH_3 > OCH_3 > CF$

6. The major product formed in the following reaction is



7. The major product formed in the following reaction is



8. Structure of the intermediate A and the final product B in the following reaction sequence are (dba = dibenzylidene acetone)

9. For the four reactions given below, the rates of the reactions will vary as

1.
$$O_2N$$
 \longrightarrow O_2N \longrightarrow O_2N

2.
$$H \longrightarrow 0$$
 $N \oplus N \oplus N \oplus N$



- A. (1) > (2) and (3) > (4)
- B. (2) > (1) and (3) > (4)
- C. (2) > (1) and (4) > (3)
- D. (1) > (2) and (4) > (3)
- 10. The intermediate that leads to the product in the following transformation is

$$\begin{array}{c|c}
\hline
& TI(NO_3)_3 \\
\hline
& CH_3OH
\end{array}$$

$$\begin{array}{c}
OCH_3 \\
OCH_3
\end{array}$$

$$A. \qquad H \\
\hline
& TI(NO_3)_2$$

B.

H

OCH₃

TI(NO₂)₂



Answers						
1. A	2. C	3. C	4. A	5. A	6. B	7. C
8. A	9. D	10. B				

Solutions

Solution 01:

This reaction involves benzyne formation. NaNH₂ being a strong base will first abstract a proton of a carbon adjacent to the leaving group leading to the formation of benzyne intermediate when chloride ion leaves.

There is possibility of attack on both the sides of the intermediate formed so we will get two products.

Path 1 gives 3-aminopyridine and path 2 gives 4-aminipyridine.

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Solution 02:

Aqueous Ag₂O gives OH⁻ ions and Ag⁺ ions.

Water attacks on the cyclopropane ring which results in the ring opening. OMe donate electron to the ring which results in the formation of new ring and removal of iodide. Further, OH gives back the electron to cylopropane ring which results in ring opening and formation of product.



Solution 03:

OH will take up the proton of HBr leading to the removal of water molecule and formation of carbocation which is stabilized by the adjacent cyclopropyl ring followed by the attack of bromide ion on carbocation.

Solution 04:

Frontier molecular orbitals represent HOMO and LUMO. HOMO is an electron donating while LUMO is electron accepting. When the interactions between HOMO and LUMO takes place, both chemical reactions and resonance concept can be explained. Now, frontier orbital interaction of carbocation intermediate for reaction between isobutylene and HCl can be represented as:

$$H - Cl$$
 $H - Cl$
 $H -$

Solution 05:

$$Z \xrightarrow{NO_2} Br + H - N \xrightarrow{NO_2} Z \xrightarrow{NO_2} Br$$

z = more electron withdrawing group, stabilize the carbanion, more will be rate constant. Electron Withdrawing Effect: CF₃ > CH₃ > OMe



Solution 06:

$$H_3C$$
 H_3C
 H_3C
 H_3CS
 H_3CS
 H_3CS
 H_3CS
 H_2C
 H_2

The lone pair on S attacks on the electrophilic carbon and iodine leaves. Further tertiary butoxide takes up the proton and creates a carbanion. The carbanion thus formed attacks on the double bond present in ring.

Solution 07:

Its Cimiacin – Dentdest Reduction

Step 1: Formation of Carbene

Step 2: Abstraction of -NH proton of indole by MeLi which results in the formation of lithium salt

Step 3: Insertion of carbene to ring of lithium salt of indole



Solution 08:

The reaction sequence of the given reaction can be represented as follows:

$$= \bigcap_{O} \frac{\operatorname{Pd(dba)_2}}{\operatorname{Ho}} \operatorname{Ho} \longrightarrow \operatorname{Ho} \longrightarrow \operatorname{Ho} \longrightarrow \operatorname{Pd} \longrightarrow \operatorname{Ho} \longrightarrow \operatorname{Pd} \longrightarrow \operatorname{Pd}$$

Solution 09:

This group's –R effect increases intermediate stability. In that situation, the electron-withdrawing group speeds up the reaction. It stabilizes the negative charge by delocalization.

A carbocation is formed here so EWG decrease the stability of carbocation. They withdraw away the electron density thus destabilizing it.



Solution 10:

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

First $Ti(NO_3)$ forms a 3-membered cyclic transition state with double bond of the cyclohexane ring. MeOH then attacks on the ring and opens the cyclic ring formed. After ring flipping, OMe attacks on to the ring forming a 5-membered ring with the removal of $Ti(NO_2)_2$. Then MeOH attacks on the carbon oxygen double bond and complete the reaction.





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