





HALOGEN DERIVATIVES

PREVIOUS QUESTIONS

1. The synthesis of alkyl fluorides is best accomplished by:
(JEE MAINS-2015)

1) Free radical fluorination

2) Sandmeyer's reaction

3) Finkelstein reaction

 4) Swarts reaction

2. In the following sequence of reactions :



1) $C_6H_5 COOH$

2) $C_6H_5 CH_3$

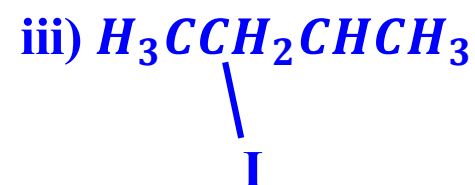
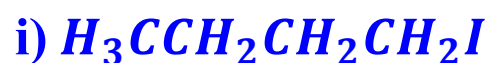
3) $C_6H_5 CH_2OH$

✓ 4) C_6H_5CHO

Solution :



3. The correct order of reactivity of the following iodides in S_N2 reaction



1) (i) > (ii) > (iii)

✓ 2) (i) > (iii) > (ii)

3) (ii) > (i) > (iii)


4) (ii) > (iii) > (i)

4. In a nucleophilic substitution reaction :

$\text{R} - \text{Br} + \text{Cl}^- \xrightarrow{\text{DMF}} \text{R} - \text{Cl} + \text{Br}^-$, which one of the following undergoes complete inversion of configuration?

[J.M.O.L-2014]

1) $\text{C}_6\text{H}_5\text{CHC}_6\text{H}_5\text{Br}$

 2) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

3) $\text{C}_6\text{H}_5\text{CHCH}_3\text{Br}$

4) $\text{C}_6\text{H}_5\text{CCH}_3\text{C}_6\text{H}_5\text{Br}$

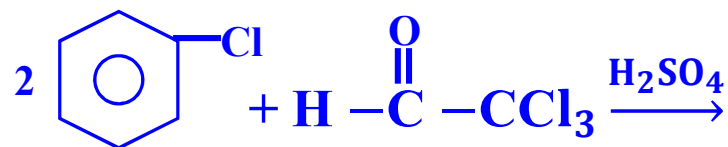
Solution :

Alkyl halide with less no. of Alkyl (or) Aryl groups gives more inversion product

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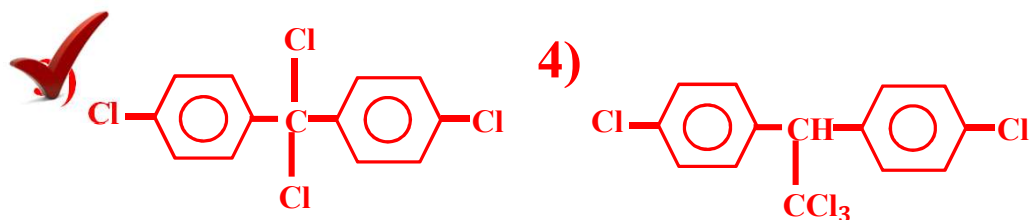
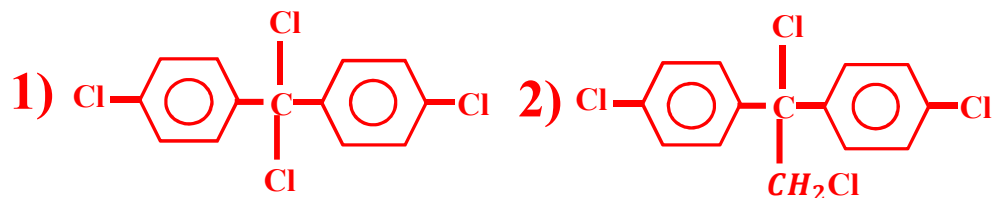
Previous

5. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4



[J.M.O.L-2014]

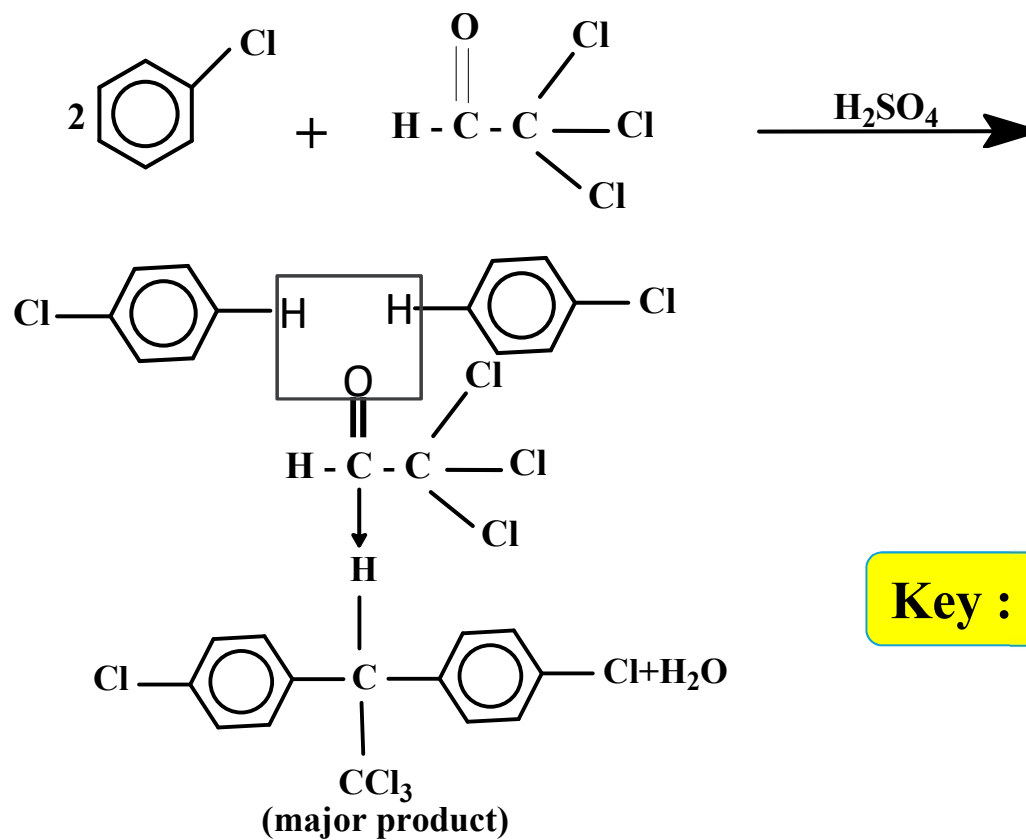
The major product formed is



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Solution :

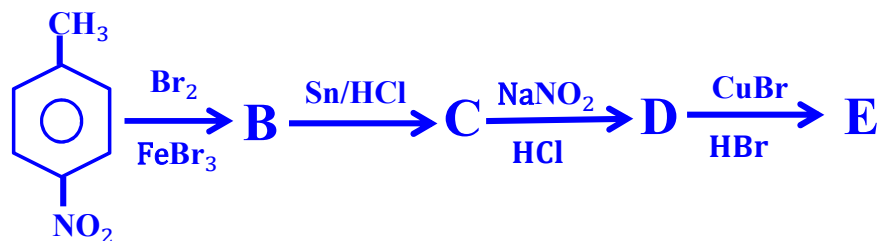


Key : 4

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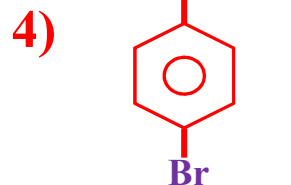
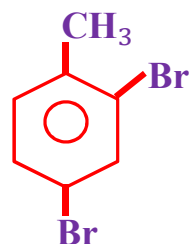
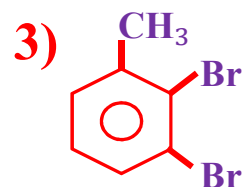
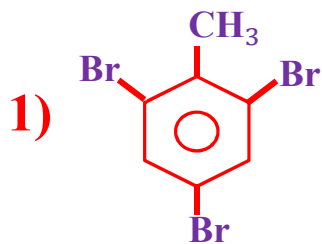
Previous

6. In a set of reactions *p* – nitro toluene yielded a product E



[J.M.O.L-2014]

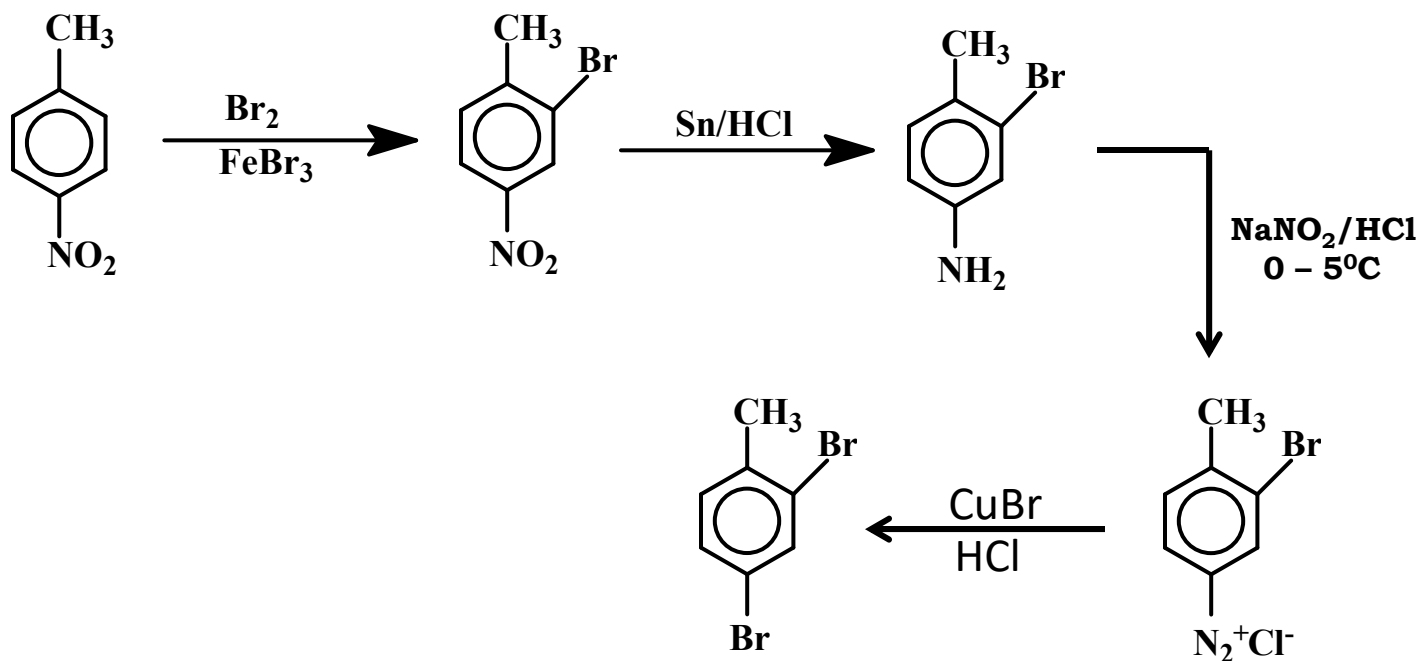
The product E would be :



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Solution :



Key : 2

7. In SN^2 reactions, the correct order of reactivity for the following compounds: CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CHCl}$ and $(\text{CH}_3)_3\text{CCl}$ is

[JEEMAINS-2014]

1) $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$

 2) $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

3) $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

4) $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$

Solution :

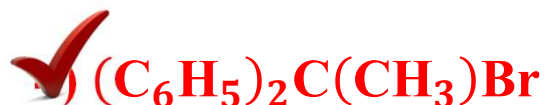
$$\text{Rate of } SN^2 \propto \frac{1}{\text{steric hinderance}}$$

The order of reactivity towards SN^2 reaction for alkyl halide is

Primary halides > secondary halides > tertiary halides

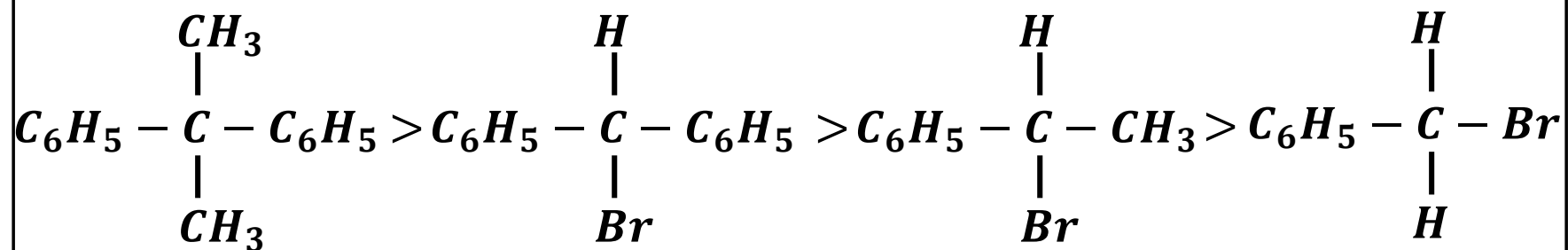
Key : 2

8. Which one of the following is more readily hydrolysed by $\text{S}_{\text{N}}1$ mechanism? [E-2014]



Solution :

The order of reactivity of halides towards SN^1 reaction :
benzyl $>$ allyl $>$ $3^\circ > 2^\circ > 1^\circ >$ methyl



Key : 4

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9. Aryl fluoride may be prepared from diazonium chloride using :

[JEE MAINS ONLINE-2013]

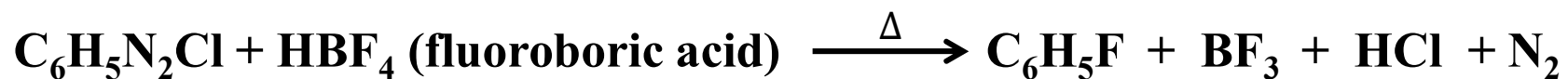
1) $\text{HBF}_4/\text{NaNO}_2, \text{Cu}, \Delta$

✓ 2) HBF_4/ Δ

3) CuF / HF

4) Cu / HF

Solution :



10. The order of reactivity of the given haloalkanes towards nucleophile is:



1) $\text{RI} > \text{RBr} > \text{RCI}$

[JEE MAINS ONLINE-2013]

2) $\text{RCI} > \text{RBr} > \text{RI}$

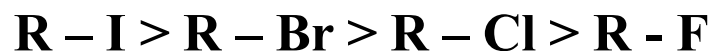
3) $\text{RBr} > \text{RCI} > \text{RI}$

4) $\text{RBr} > \text{RI} > \text{RCI}$

Solution :

The order of reactivity of haloalkanes towards a nucleophile depends upon the $\text{R} - \text{X}$ bond dissociation energy.

Therefore it depends upon the size of the halide ion or $\text{C} - \text{X}$ bond length



11. In nucleophilic substitution reaction, order of halogens as incoming (attacking) nucleophile is: $I^- > Br^- > Cl^-$

The order of halogens as departing nucleophile should be:



[JEE MAINS ONLINE-2013]



Solution :

Bigger the size and lower the electronegativity easier the nucleophilic substitution.

Therefore the order of leaving group : $I^- > Br^- > Cl^-$

12. Heating chloroform with aqueous sodium hydroxide solution forms:

[E-2013]

1) Sodium acetate

2) Sodium oxalate

 **3) Sodium formate**

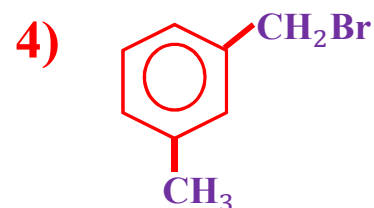
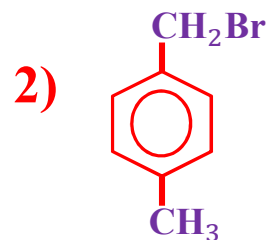
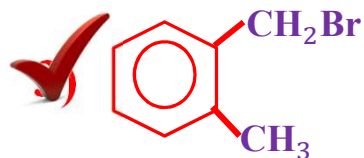
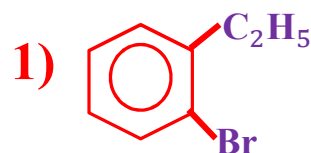
4) Chloral

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13. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating, Identify the compound (A).

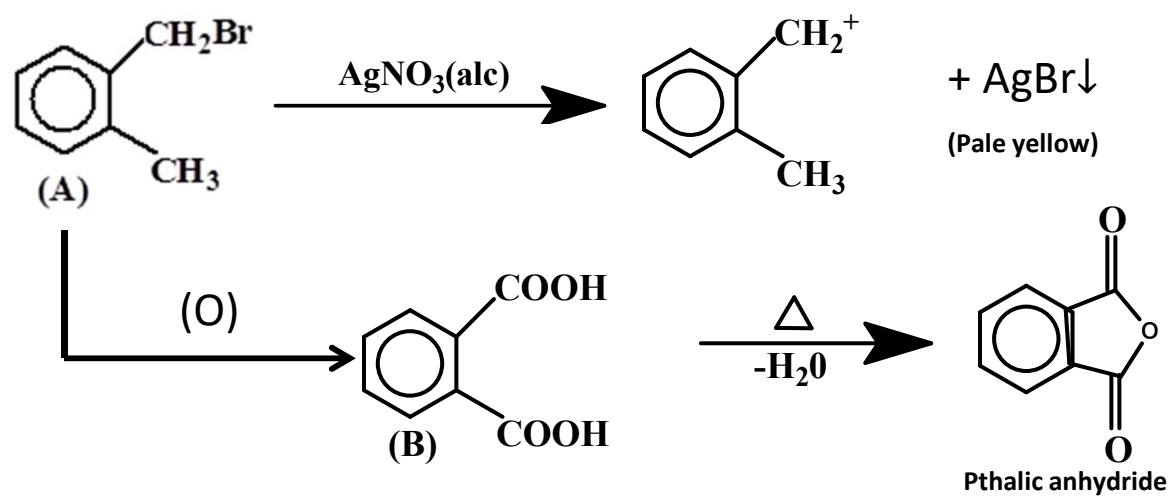
[JEEMAINS-2013]



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Solution :



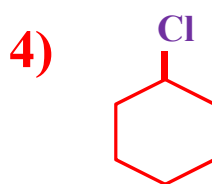
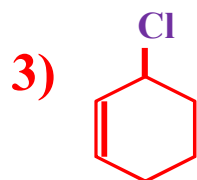
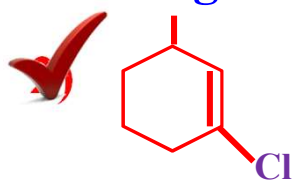
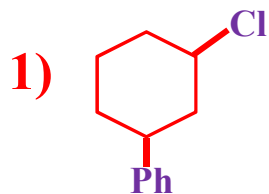
Key : 3

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14. Which one of the following is most stable?

[J.M.O.L-2013]



Solution :

allylic carbon attachment due to stable carbocation formation.

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15. For the compounds CH_3Cl , CH_3Br , CH_3I and CH_3F , the correct order of increasing C-X bond length is : [2012]

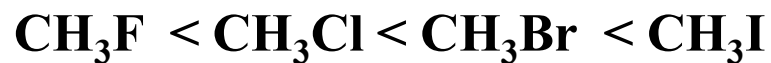
✓ 1) N

2) S

3) Cl

4) C and H

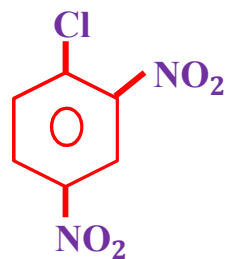
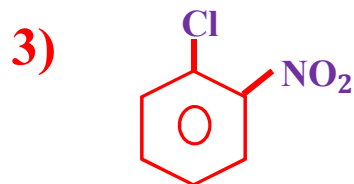
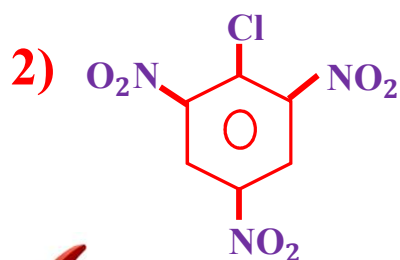
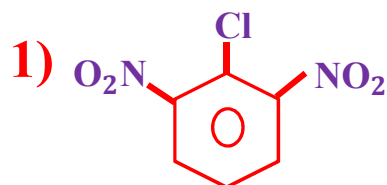
Solution :



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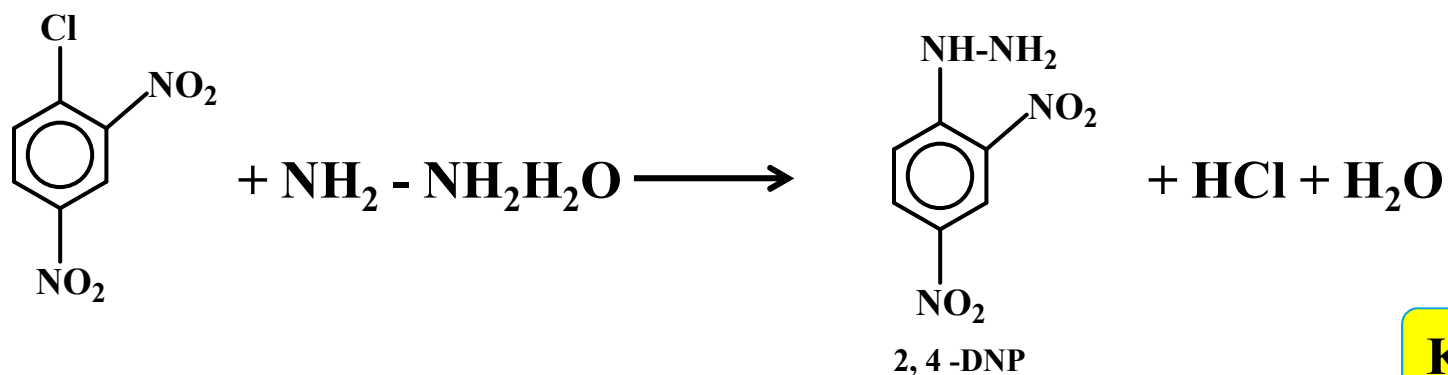
Previous

16. A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the following ? [2012]



Solution :

Borsch reagent is 2, 4- DNP (2, 4- dinitrophenylhydrazine)

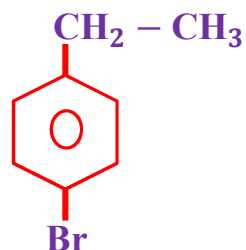


Key : 4

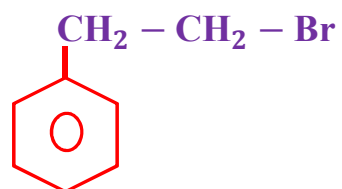
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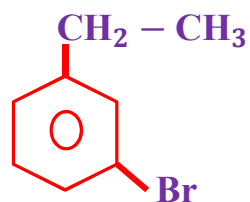
17. The product of the reaction b/w ethyl benzene and N-bromo succinimide is [2012]



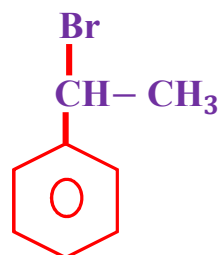
2)



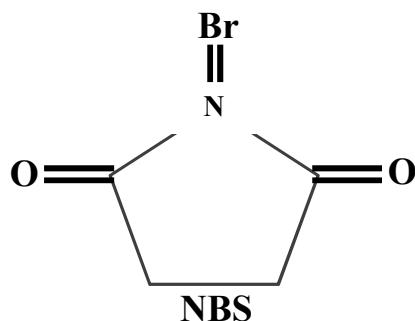
3)



4)



Solution :

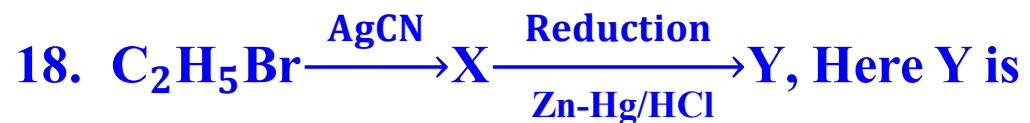


NBS is a brominating agent that replaces H atom in benzylic or allylic position

Key : 4

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[2011]

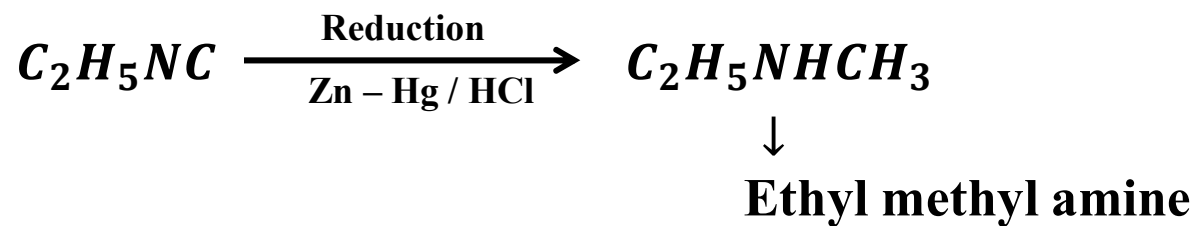
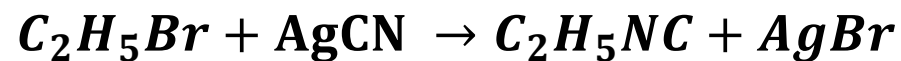
1) n-propyl amine

2) Ethyl amine

3) Isopropyl amine

 4) Ethyl methyl amine

Solution :



Key : 4

19. Which of the following statements is wrong?

[2011]



1) The reaction methyl magnesium bromide with acetone gives butanol -2

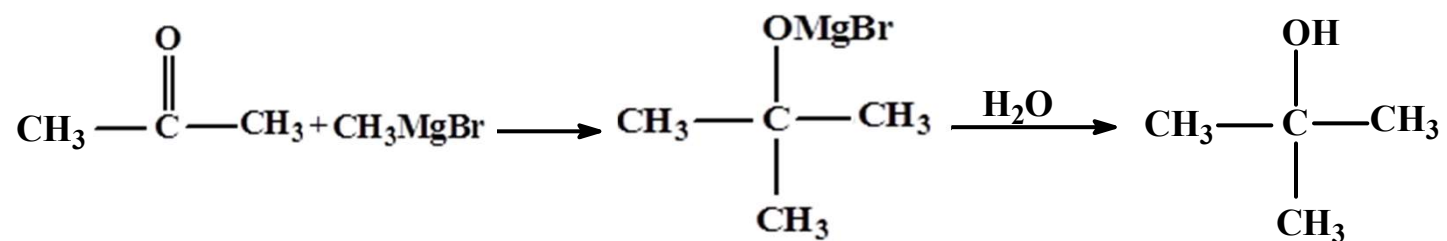
2) Alkyl halides follow the following reactivity sequences on reaction with alkenes : $R-I > R-Br > R-Cl > R-F$

3) $C_2H_4Cl_2$ may exist in two isomeric forms

4) Ethyl chloride on reduction with Zn-Cu couple and alcohol gives ethane.

Solution :

Acetone on action of methyl magnesium bromide followed by hydrolysis gives 3^o butyl alcohol.



Key : 1

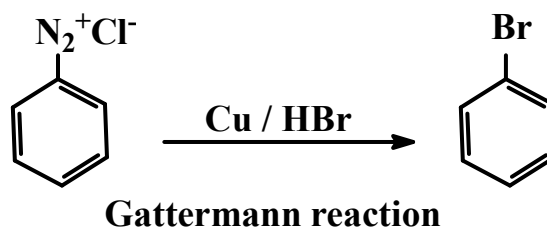
HALOGEN DERIVATIVES

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20. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by: [2011]

- ✓ 1) Gattermann reaction
- 2) Azo coupling reaction
- 3) Fiedal – crafts reaction
- 4) Remer-Tierner reaction

Solution :



21. Beilstein test is used for estimation of which one of following elements
[2011]

1) CH_3F , CH_3Cl , CH_3Br , CH_3I

2) CH_3F , CH_3Br , CH_3Cl , CH_3I

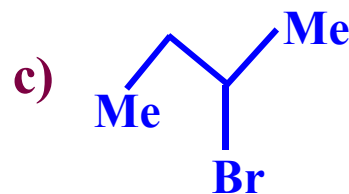
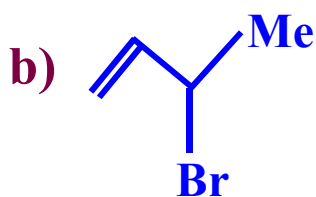
 3) CH_3F , CH_3I , CH_3F , CH_3I

4) CH_3Cl , CH_3Br , CH_3F , CH_3I

HALOGEN DERIVATIVES

Previous

22. Consider the following bromides :



[A-2010]

The correct order of SN^1 reactivity is



1) $B > C > A$

2) $B > A > C$

3) $C > B > A$

4) $A > B > C$

Solution :

Order of reactivity of various Alkyl halides towards SN^1 reaction is

Benzyl halide > Allyl halide > Tertiary alkyl halide > Secondary alkyl halide > Primary alkyl halide

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23. Consider the following reaction, $\text{C}_2\text{H}_5\text{Cl} + \text{AgCN} \xrightarrow{\text{EtOH}/\text{H}_2\text{O}} \underline{\text{X}}$ (major).
Which one of the following statements is true for X [E-2009]

I) It gives propionic acid on hydrolysis

II) It has an ester functional group

III) It has a nitrogen linked to ethyl carbon

IV) It has a cyanide group

1) IV

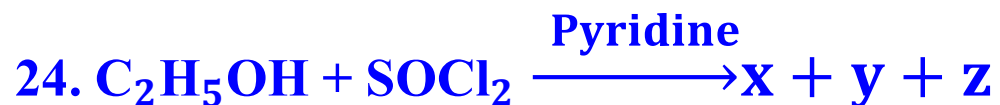
 2) III

3) II

4) I

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In this reaction x, y and z respectively are

[E-2008]

1) $\text{C}_2\text{H}_4\text{Cl}_2, \text{SO}_2, \text{HCl}$

 2) $\text{C}_2\text{H}_5\text{Cl}, \text{SO}_2, \text{HCl}$

3) $\text{C}_2\text{H}_5\text{Cl}, \text{SOCl}, \text{HCl}$

4) $\text{C}_2\text{H}_4, \text{SO}_2, \text{Cl}_2$

Solution :



$\text{x} \rightarrow \text{C}_2\text{H}_5\text{Cl}$

$\text{y} \rightarrow \text{SO}_2$

$\text{z} \rightarrow \text{HCl}$

25. The organic chloro compound, which shows complete stereochemical inversion during a SN^2 reaction, is [A-2008]



Solution :

Nucleophilic substitution bimolecular (SN^2) prefers less sterically hindered site to attack.

**Lesser the steric hindrance better the SN^2 reaction.
So ease of reaction is $1^\circ > 2^\circ > 3^\circ$.**

Key : 4

26. Identify 'B' in the following reaction



[E-2007]

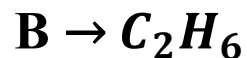
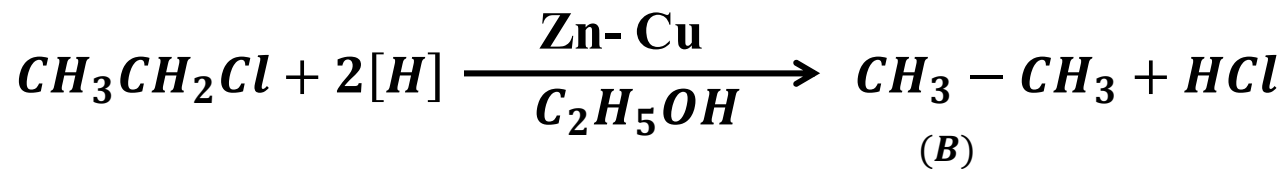
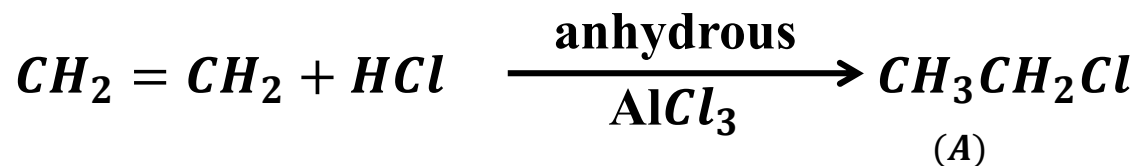
1) CH₄

✓ 2) C₂H₆

3) C₂H₅Cl

4) C₂H₅OH

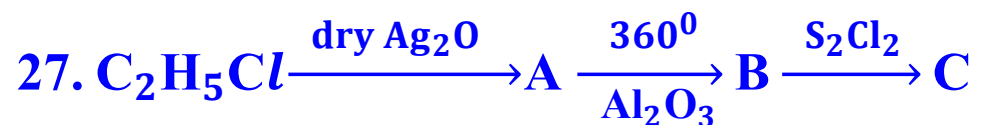
Solution :



Key : 2

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In the above sequence of reactions identify 'C'

[E-2007]

1) Chloretone

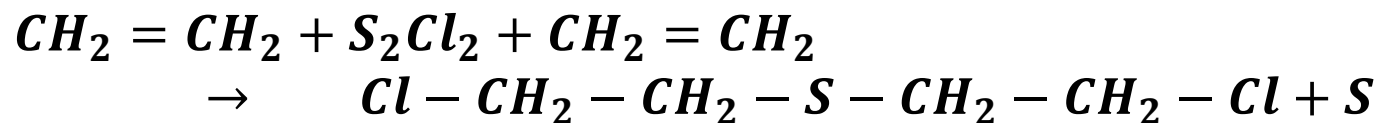
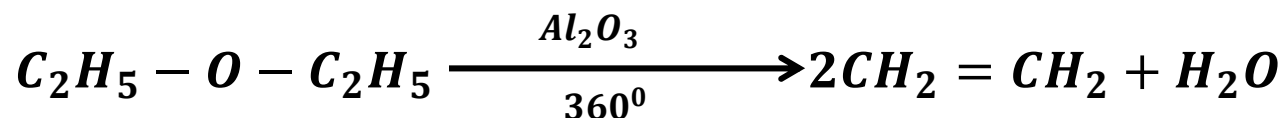
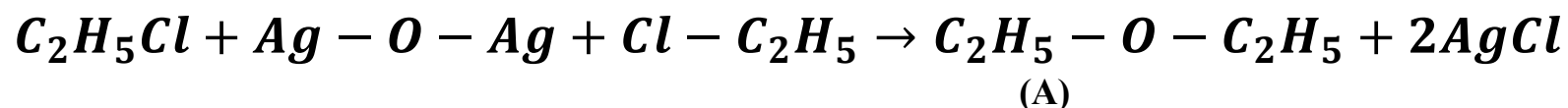
2) Chloropicrin



3) Mustard gas

4) Lewisite gas

Solution :



↓
Mustard gas

Key : 3

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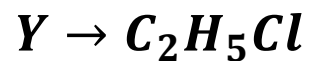
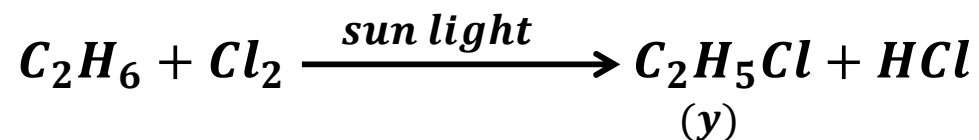
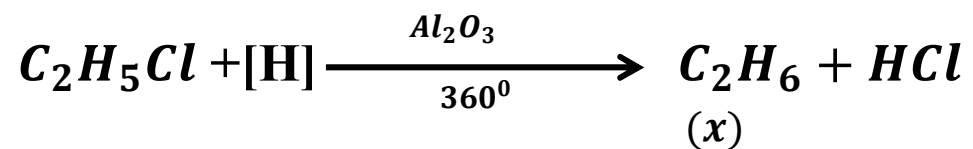
Previous

28. Ethyl Chloride on reduction with LiAlH_4 gives compound 'X' as important product, 'X' on chlorination with one mole of Cl_2 in the presence of light at ordinary temperature gives Y, what is 'Y'?

[E-2007]



Solution :



Key : 3

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29. On treatment of toluene with Cl_2 in presence of Fe, dark the product formed is [A-2007]



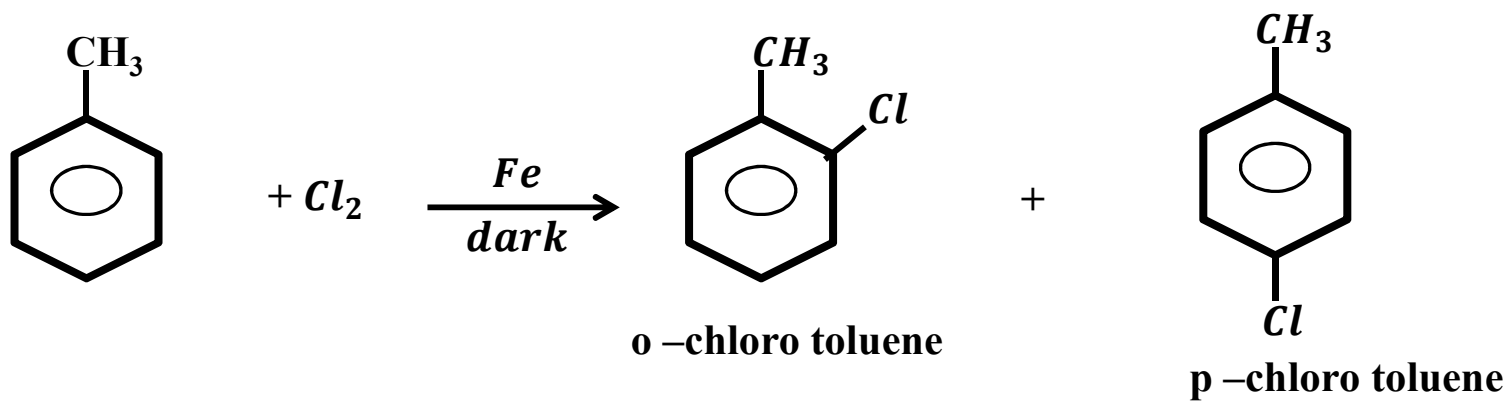
1) o- and p-chloro toluene

2) benzyl chloride

3) m-chloro toluene

4) only p-chloro toluene

Solution :



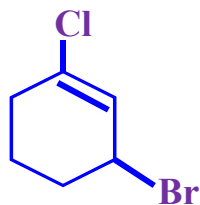
Key : 1

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30. The IUPAC name of the compound shown below is

[A-2006]



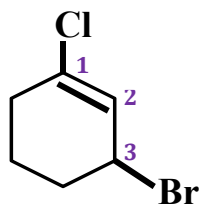
1) 2-bromo-6-chloro cyclohexene -1-ene

2) 6-bromo-2-chloro cyclohexene

✓ 3) 3-bromo-1-chloro cyclohexene

4) 1-bromo-3-chloro cyclohexene

Solution :



3-bromo-1- chloro cyclohexene

Key : 3

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31. Which of the following can give a Grignard reagent when reacted with magnesium in dry ether ? [E-2006]

1) C_2H_6



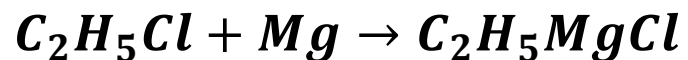
2) C_2H_5Cl

3) C_2H_5OH

4) C_2H_5CN

Solution :

Alkyl halide reacts with Mg metal to form Grignard reagent



32. Which of the following reagents when heated with ethyl chloride forms ethylene [E-2006]

1) Aqueous KOH

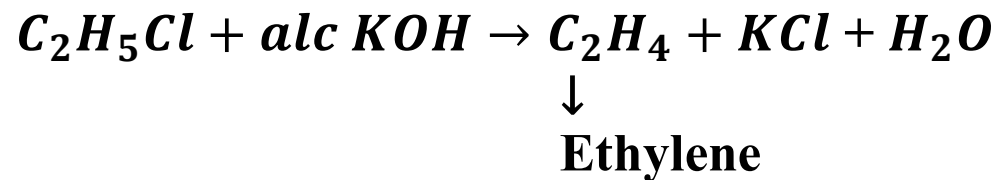
2) Zn/HCl



3) Alcoholic - KOH


4) HI

Solution :

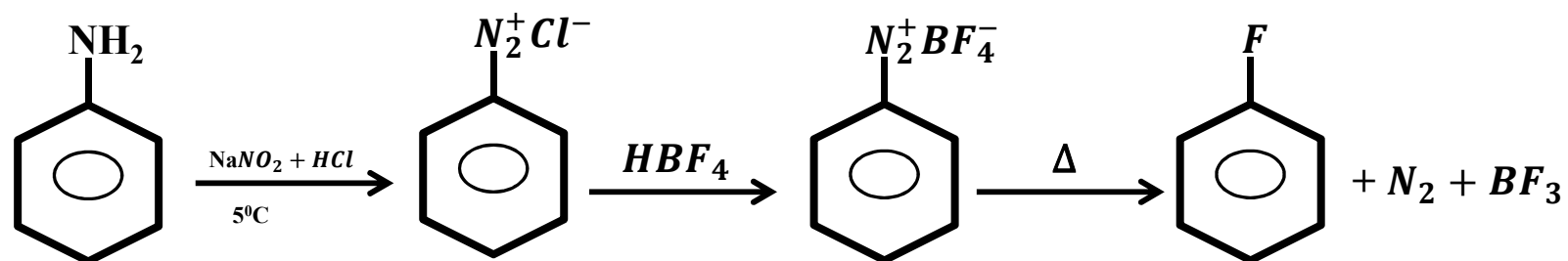


33. Fluorobenzene ($\text{C}_6\text{H}_5\text{F}$) can be synthesized in the laboratory.

[A-2006]

- 1) by heating phenol with HF and KF**
-  **2) from aniline by diazotisation followed by heating the diazonium salt with HBF_4**
- 3) by direct fluorination of benzene with F_2 gas**
- 4) by reacting bromobenzene with NaF solution**

Solution :



Key : 2

HALOGEN DERIVATIVES

Previous

34. $\text{CH}_3\text{Br} + \text{N}\bar{\text{u}} \rightarrow \text{CH}_3 - \text{Nu} + \text{Br}^-$ the decreasing order of the rate of above reaction with nucleophiles ($\text{N}\bar{\text{u}}$) A to D is

$[\text{N}\bar{\text{u}} = (\text{A})\text{PhO}^-, (\text{B})\text{CH}_3\text{COO}^-, (\text{C})\text{HO}^-, (\text{D})\text{CH}_3\text{O}^-]$

[A-2006]



1) $\text{D} > \text{C} > \text{A} > \text{B}$

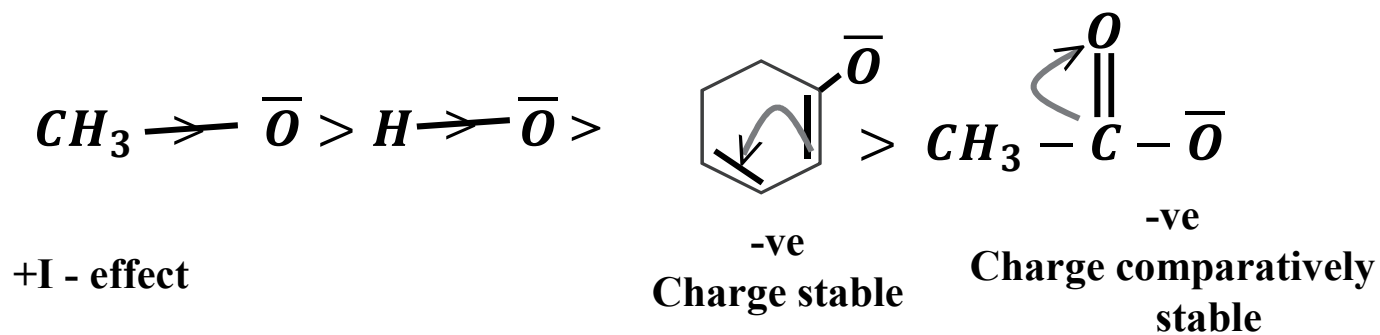
2) $\text{D} > \text{C} > \text{B} > \text{A}$

3) $\text{A} > \text{B} > \text{C} > \text{D}$

4) $\text{B} > \text{D} > \text{C} > \text{A}$

Solution :

Nucleophilicity order is



Key : 1

35. Tertiary alkyl halides are particularly substituted by SN^2 mechanism because of [E-2005]



1) Steric hindrance

2) Inductive effect

3) Instability

4) Insolubility

HALOGEN DERIVATIVES

Previous

36. Identify A and B in the following reactions:

[E-2005]



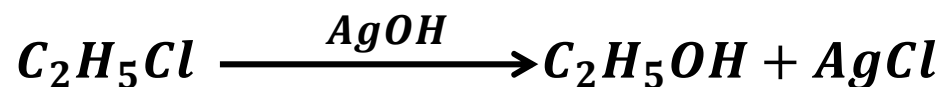
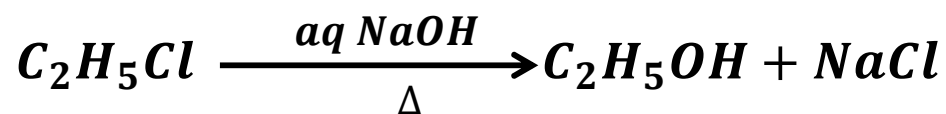
1) A = C₂H₂, B = C₂H₆

2) A = C₂H₅Cl, B = C₂H₄

3) A = C₂H₄, B = C₂H₅Cl

✓ 4) A = C₂H₅Cl, B = C₂H₅Cl

Solution :



HALOGEN DERIVATIVES

Previous

37. What is the molecular formula of the product formed when Benzene is reacted with ethyl chloride in presence of anhydrous aluminium chloride. [E-2004]

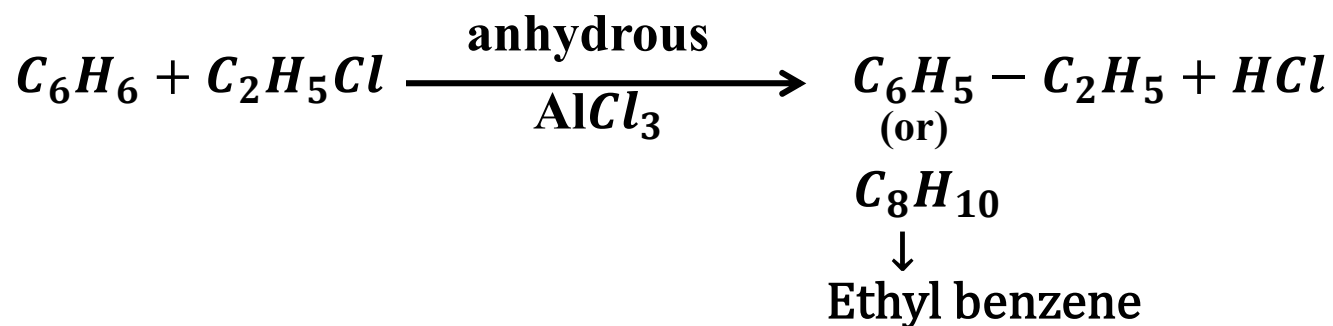
✓ 1) C_8H_{10}

2) C_6H_6

3) C_8H_8

4) C_6H_5Cl

Solution :



HALOGEN DERIVATIVES

Previous

38. Identify A and B in the following reaction

[E-2004]

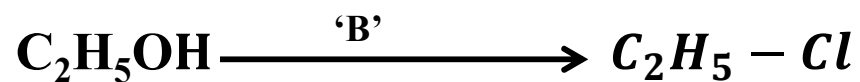
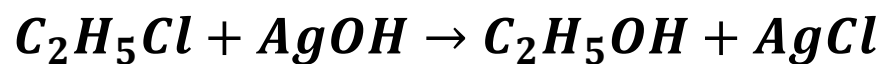


1) A = aq.KOH, B = AgOH

2) A = alc.KOH, B = aq.NaOH

3) A = aq.NaOH, B = AgNO₂

4) A = AgNO₂, B = KNO₂

Solution :**Key : 1**

39. The reagent used for converting benzene to ethyl benzene is.

[M-2004]



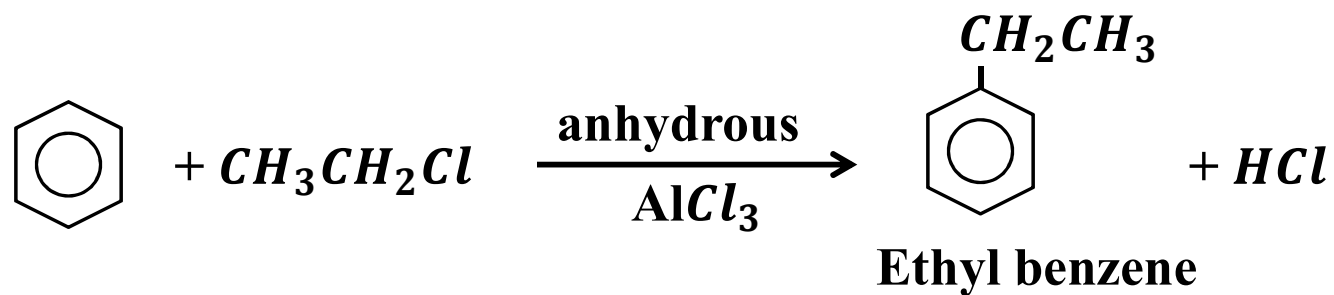
1) $\text{C}_2\text{H}_5\text{Cl}$, anhydrous AlCl_3

2) $\text{C}_2\text{H}_5\text{Cl}$, aq AlCl_3

3) $\text{C}_2\text{H}_5\text{OH}$, anhydrous AlCl_3

4) $\text{C}_2\text{H}_5\text{Cl}$, SOCl_2

Solution :

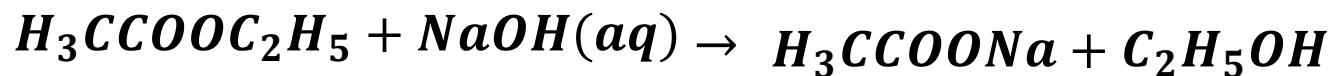


Key : 1

40. On mixing ethyl acetate with aqueous NaOH the products formed
[A-2004]



Solution :



HALOGEN DERIVATIVES

Previous

41. Bottles containing $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ lost their original labels. They were labelled A and B for testing A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some AgNO_3 solution added. Solution B gave a yellow precipitate. Which one of the following statements is true for the experiment?

[A-2003]

1) Addition of HNO_3 was unnecessary

 2) A was $\text{C}_6\text{H}_5\text{I}$

3) A was $\text{C}_6\text{H}_5\text{CH}_2\text{I}$

4) B was $\text{C}_6\text{H}_5\text{I}$

42. Heating chloroethane with ---- yields a product containing isocyanide group. [M-2002]

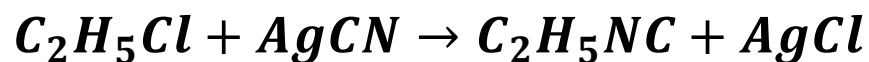
✓ 1) AgCN

2) KCN

3) HCN

4) HNO₃

Solution :



Ethyl Iso cyanide

HALOGEN DERIVATIVES

Previous

43. What is X in the following reaction

[M-2001]



1) KHCO_3

2) alc. KOH

 3) aq. KOH

4) K_2CO_3

Solution :



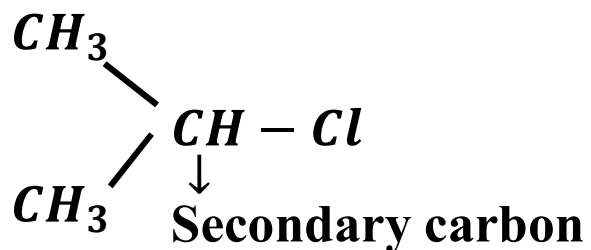
If alkyl halide reacts with aq.KOH Nucleophilic substitution reaction takes place

If alkyl halide reacts with alc.KOH Elimination reaction takes place

44. Which one of the following is a secondary alkyl halide

- 1) $(\text{CH}_3)_3\text{CCl}$ 2) $\text{C}_2\text{H}_5\text{Cl}$  3) $(\text{CH}_3)_2\text{CHCl}$ 4) $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$

Solution :




If halogen is attached to 2° carbon is called secondary alkyl halide

45. Chloro ethane reacts with X to form diethyl ether. What is X ?

[E-2001]

1) NaOH

2) H_2SO_4

 3) $\text{C}_2\text{H}_5\text{ONa}$

4) $\text{Na}_2\text{S}_2\text{O}_3$

Solution :





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