BYJU'S Study Planner for Board Term I
(CBSE Grade 12)

Date: 10/11/2021

Subject: Chemistry

Topic : Haloalkanes and Haloarenes

Class: Standard XII

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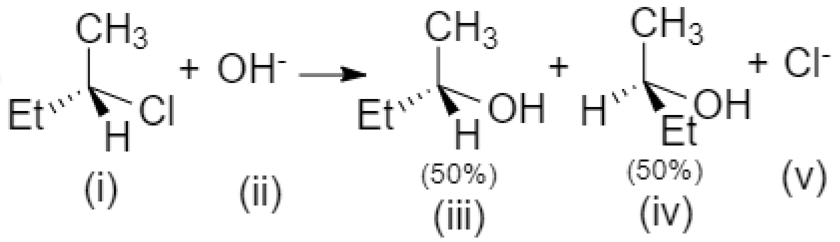
1. Alcohols can be prepared by haloalkanes using hydroxide ion in aqueous media through S_N1 and S_N2.

The S_N1 reaction is a two-step reaction. In the first step, the carbon-halogen bond breaks to generate a stable carbocation. In the second step, the nucleophile reacts rapidly with the carbocation. This reaction follows first order kinetics.

The S_N2 is a concerted reaction in which transition state is achieved where bond making and bond breaking occur simultaneously. This reaction follows second order kinetics.

Consider the following reaction sequence.



Which of the following statement is correct about the mechanism of this reaction?

✔ **A.** A carbocation will be formed as an intermediate in the reaction

✖ **B.** OH^- will attach the substrate (i) from one side and Cl^- will leave it simultaneously from other side

✖ **C.** An unstable intermediate will be formed in which OH^- and Cl^- will be attached by weak bonds

✖ **D.** Reaction proceeds through E_1 mechanism

Reaction proceeds in two steps. In step I, the polarised $C-Cl$ bond undergoes slow cleavage to produce a carbocation and a chloride ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.
It can be estimated that the reacrtion may proceed either through S_N1 or S_N2 type. Since in the prodcut, the spatial arrangement of bonds to the carbon centre are preserved which that the reaction is followed by S_N1 mechanism.

2. Alcohols can be prepared by haloalkanes using hydroxide ion in aqueous media through S_N1 and S_N2.

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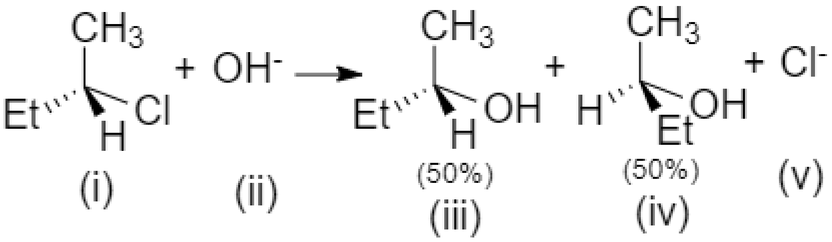

Which of the following statement is correct about the kinetics of this reaction?

✗ **A.** The rate of reaction depends on the concentration of only (ii)

✓ **B.** The rate of reaction depends on the concentration of only (i)

✗ **C.** The rate of reaction depends on concentration of both (i) and (ii)

✗ **D.** The rate of reaction is independent of concentration of both (i) and (ii)

Reaction follows S_N1 pathway. Step I is the slowest and reversible since formation of carbocation takes place. The rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.

3. Alcohols can be prepared by haloalkanes using hydroxide ion in aqueous media through S_N1 and S_N2.

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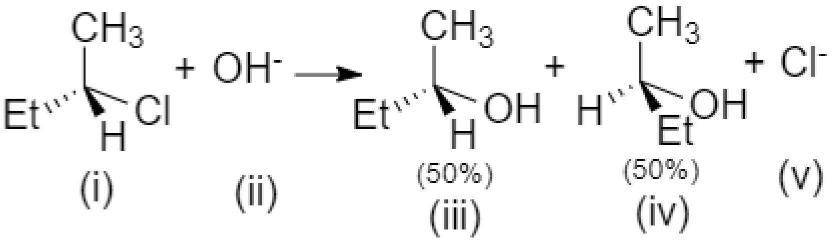
Consider the following reaction sequence.



Which of the following statement is correct about regarding the reaction?

✗ **A.** Molecularity of the reaction is two

✓ **B.** Polar protic solvents drive this reaction

✗ **C.** Polar aprotic solvents are preferred

✗ **D.** None of these

Reaction follows S_N1 pathway. Step I is the slowest and reversible since formation of carbocation takes place. The rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Molecularity of the reaction is one.

Polar protic solvents are used in S_N1 reaction. Ex- water, alcohol

4. Which of the following analogies is correct?

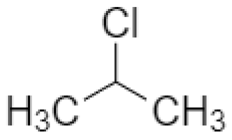
Isopropyl chloride : 2^oalkyl halide :: Isobutyl chloride :

✓ **A.** 1^oalkyl halide

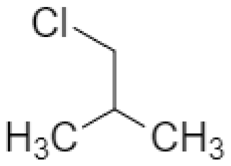
✗ **B.** 2^oalkyl halide

✗ **C.** 3^oalkyl halide

✗ **D.** None of these



isopropyl chloride



isobutyl chloride

In isopropyl chloride, the chlorine is attached to a carbon that is only attached to two other carbon hence it is secondary halide. Whereas in isobutyl chloride, the chlorine is attached to a carbon that is only attached to one other carbon hence it is primary alkyl halide.

5.

Column - I	Column - II
(i) S_N1 reaction	(A) *vic* -dihalide
(ii) Alkylidene halides	(B) *gem* -dihalide
(iii) Bromination	(C) Racemisation
(iv) Elimination of HX	(D) Saytzeff rule

Which of the following is the best matched option?

✗ **A.** i-C, ii- D, iii- A, iv-B

✓ **B.** i-C, ii- B, iii- A, iv-D

✗ **C.** i-D, ii- B, iii- A, iv-C

✗ **D.** i-D, ii- A, iii- B, iv-C

(i) Racemisation takes place in S_N1 reaction.
(ii) Alkylidene halides are named as gemdihalides. In gemdihalides halogen atoms are present on same carbon atom.
(iii) In vicinal dihalides, halogen atoms are present on the adjacent carbon atom. Bromination of alkenes will give vicinal dihalides.
(iv) Elimination of HX from allrylhalide follows Saytzeff rule.

6. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): It is difficult to replace chlorine by $-OH$ in chlorobenzene in companion to that in chloroethane.
Reason (B): chlorine carbon $(C-Cl)$ bond in chlorobenzene has a partial double bond character due to resonance.

- ✓ **A.** Both A and R are true and R is the correct explanation of A
- ✗ **B.** Both A and R are true but R is not the correct explanation of A
- ✗ **C.** A is true but R is false
- ✗ **D.** A is false but R is true

Assertion and reason both are correct and reason is the correct explanation of assertion. It is difficult to replace chlorine by $-OH$ in chlorobenzene in comparision to that in chloroethane because $C-Cl$ bond in chlorobenzene has a partial bond character due to resonance.

7. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): S_N2 reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.
Reason (B): S_N2 reactions always proceed with inversion of configuration.

- ✗ **A.** Both A and R are true and R is the correct explanation of A
- ✗ **B.** Both A and R are true but R is not the correct explanation of A
- ✗ **C.** A is true but R is false
- ✓ **D.** A is false but R is true

Aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the $C-Cl$ bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. So assertion is false however reason is true

8. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A): Treatment of chloroethane with a saturated solution of $AgCN$ gives ethyl isocyanide as a major product.

Reason (B): Cyanide ion (CN^-) is an ambident nucleophile.

☒ **A.** Both A and R are true and R is the correct explanation of A

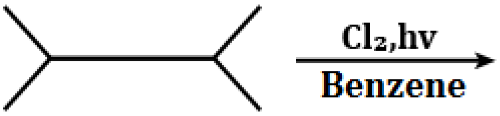
☑ **B.** Both A and R are true but R is not the correct explanation of A

☒ **C.** A is true but R is false

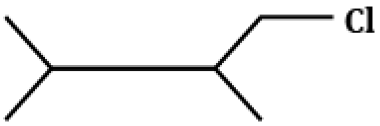
☒ **D.** A is false but R is true

Alkyl halides when react with saturated solution of $AgCN$ isocyanides are formed.
The electronegativity difference between Ag and C is so small that $Ag-C$ bond is covalent.
The carbon atom is no longer act as a nucleophile so N atom attacks and form isocyanide.
Hence assertion and reason bopth are correct statements. But reason is no the correct expalanation.

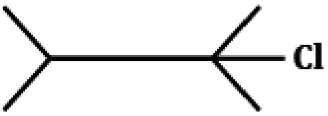
9. The major monochlorinated product in the following reaction is



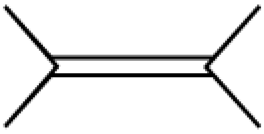
☒ **A.**



✓ **B.**



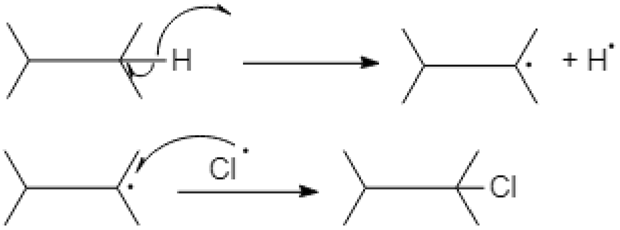
☒ **C.**



☒ **D.** None of these

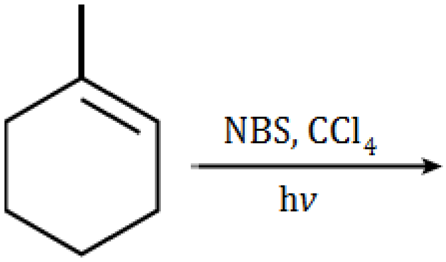
Chlorination is highly selective in nucleophilic non-polar solvents. Because it increases stability of chlorine radical. The reaction should be like

$$Cl\text{-}Cl \xrightarrow{h\nu} 2\,Cl^{\bullet}$$



The tertiary radical is the most stable.

10. The total number of structural isomers formed in the following reaction is:



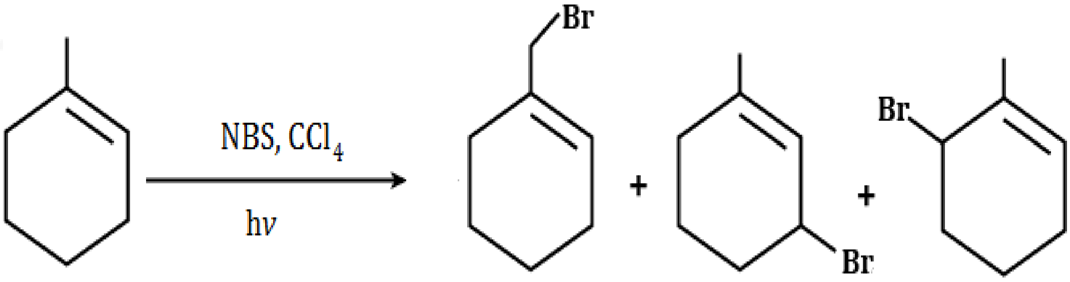
✗ **A.** 6

✗ **B.** 5

✗ **C.** 4

✓ **D.** 3

Only allylic bromination undergoes in presence of NBS. So, number of products formed is 3.



11. The correct order of increasing $C-X$ bond length is:
(R is methyl group)

✓ **A.** $RI > RBr > RCl > RF$

✗ **B.** $RF > RCl > RBr > RI$

✗ **C.** $RBr > RCl > RI > RF$

✗ **D.** $RCl > RF > RI > RBr$

$C-X$ bond length totally depends on atomic size of halogens . The more is the size more will be bond length. The atomic size of halogens is $I > Br > Cl > F$. Hence, the correct order of increasing C-X bond length is $RI > RBr > RCl > RF$.

12. The IUPAC name of $CH_2 = CH - CH_2Cl$ is

✓ **A.** 3-chloro-1-propene

✗ **B.** 1-chloro-3-propene

✗ **C.** Allyl chloride

✗ **D.** Vinyl chloride

The correct numbering of the parent chain is $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2Cl$. Halogens are always used as substituent and is present at 3rd carbon. Also one double bond is present as functional group at first carbon. Since parent chain is of 3 carbon so word root is prop. so the correct IUPAC name is 3-chloro-1-propene.

13. The reaction of $SOCl_2$ on alcohols to form alkyl chlorides gives good yields because

✗ **A.** alkyl chlorides are immiscible with $SOCl_2$

✓ **B.** by-products of the reaction are gaseous and escape out

✗ **C.** alcohol and $SOCl_2$ are soluble in water

✗ **D.** the reaction does not occur via intermediate formation of an alkyl chlorosulphite

$R - OH + SOCl_2 \rightarrow R - Cl(l) + HCl(g) + SO_2(g)$

Except the alkyl halide, by-products sulphur dioxide and hydrogen halides are gases and can be removed to make the reaction to go forward to completion. This yields a pure alkyl halide.

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14. Finkelstein reaction is

- ☒ **A.** $2CH_3CH_2Cl + Ag_2O\ (dry) \rightarrow CH_3CH_2OCH_2CH_3 + 2AgCl$
- ✓ **B.** $CH_3CH_2Br + NaI \xrightarrow{\text{Dry Acetone}} CH_3CH_2I + NaBr$
- ☒ **C.** $2CH_3CH_2Br + Ag_2O + H_2O \rightarrow 2CH_3CH_2OH + 2AgBr$
- ☒ **D.** $CH_3CH_3Cl + NaOCH_3 \rightarrow CH_3CH_2OCH_3 + NaCl$

The Finkelstein reaction is an organic reaction where an alkyl halide is converted into another alkyl halide by reacting with NaI. This reactions occurs in the presence of dry acetone because NaI is more soluble in dry acetone whereas NaCl and NaBr are precipitated out. Thus, increasing of concentration of I^- ion in the solution which favour the reaction to proceed in forward direction. The mechanism for this reaction is a simple, single-step bimolecular nucleophilic substitution reaction (S_N2) which like all S_N2 reactions occur with inversion of stereochemistry.

$$CH_3CH_2Br + NaI \xrightarrow{\text{Dry Acetone}} CH_3CH_2I + NaBr$$

15. Which one of the following is not correct order of boiling points of the alkyl halides?

✗ **A.** $CHCl_3 > CH_2Cl_2$

✗ **B.** $CH_3(CH_2)_3Cl > CH_3(CH_2)_2Cl$

✓ **C.** $(CH_3)_3CCl > (CH_3)_2CHCH_2Cl$

✗ **D.** $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3$

Intermolecular forces of attractions increases as molecular mass increases. So, large amount of heat require to break strong intermolecular forces and thus boiling point increases.

a) boiling point of $CHCl_3$ is more than CH_2Cl_2 because $CHCl_3$ has more molecular mass than CH_2Cl_2.

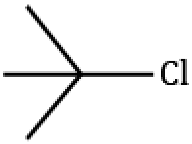
Intermolecular forces of attractions increases as molecular size increases. So, large amount of heat require to break strong intermolecular forces and thus boiling point increases.
boiling point of $CH_3(CH_2)_3Cl$ is more than $CH_3(CH_2)_2Cl$ because molecular size of $CH_3(CH_2)_2Cl$ is larger than $CH_3(CH_2)_3Cl$
Similarly, $CH_3CH_2CHClCH_2CH_3 > CH_3(CH_2)_3Cl$

Boiling point of isomeric haloalkanes decreases with increase in branching because surface area of molecule decreases due to which intermolecular forces of attraction decrease and hence boiling point decreases.
Boiling point of $(CH_3)_3CCl$ is less than $(CH_3)_2CHCH_2Cl$ as former is more branched.

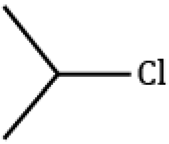
Hence, the correct answer is option (c).

16. Which of the following alkyl halide is more reactive towards $E1$ reaction?

✓ **A.**



✗ **B.**



✗ **C.**

✗ **D.** $CH_3 - Cl$

E1 reaction is a two step process.
In step 1, leaving group leaves and form a carbocation.
In step 2, the base will attack the proton and proton abstraction takes place.
Slowest step in the reaction is the rate determining step.
In E1, formation of carbocation is the slowest step. Hence, it is the rate determining step.
Thus, the rate of the reaction depends on the rate of formation of carbocation. Stable carbocation will be formed easily so rate of E1 reaction depends on the stability of the carbocation formed.

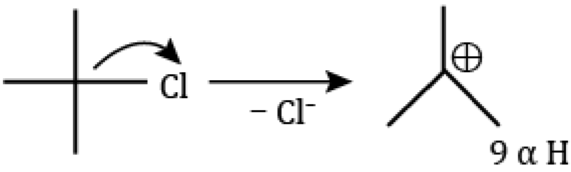
Compound (a), forms tertiary carbocation with 9 $\alpha-$ hydrogen.

Compound (b), forms secondary carbocation with 6 $\alpha-$ hydrogen.

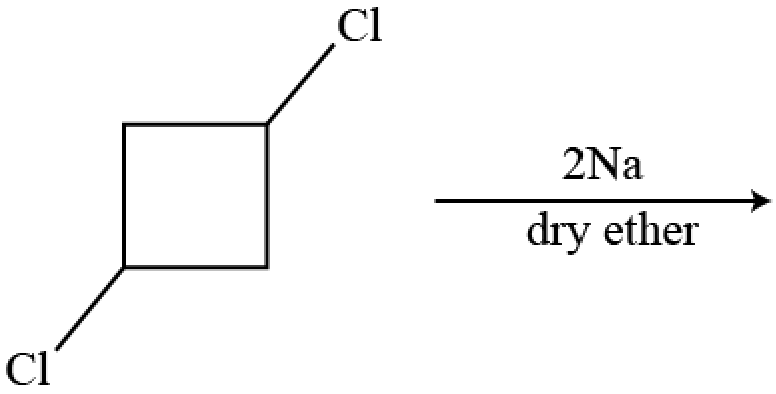
Compound (c), forms primary carbocation with 3 $\alpha-$ hydrogen.

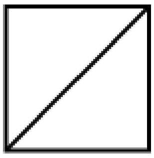
Compound (d), forms primary carbocation with no α carbon.

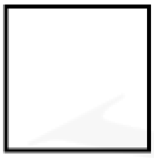
Tertiary carbocation is more stable due to +I effect and hyperconjugation effect (9 $\alpha-$ hydrogen).
Therefore, compound (a) t-butyl chloride is the most reactive alkyl halide towards $E1$ reaction.



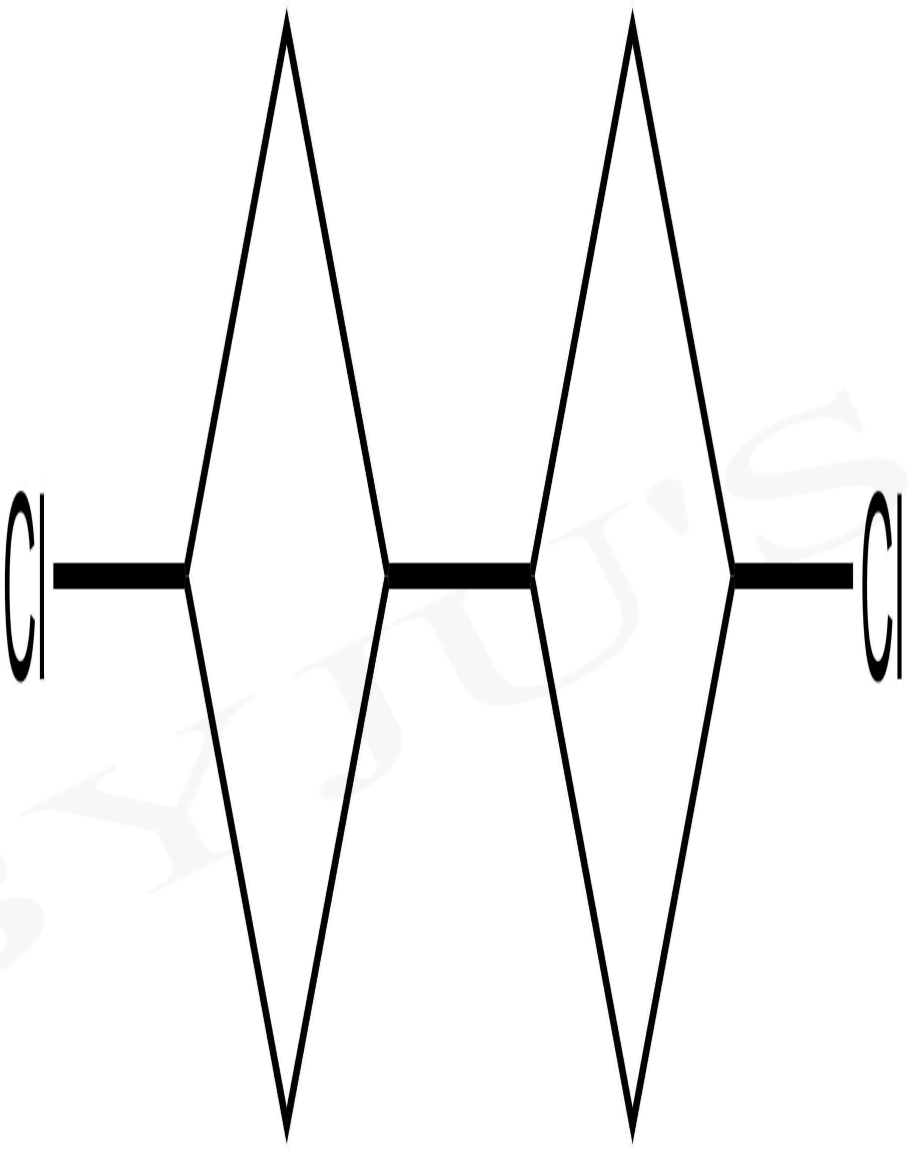
17. Find the major product for the given reaction?



✓ **A.** 

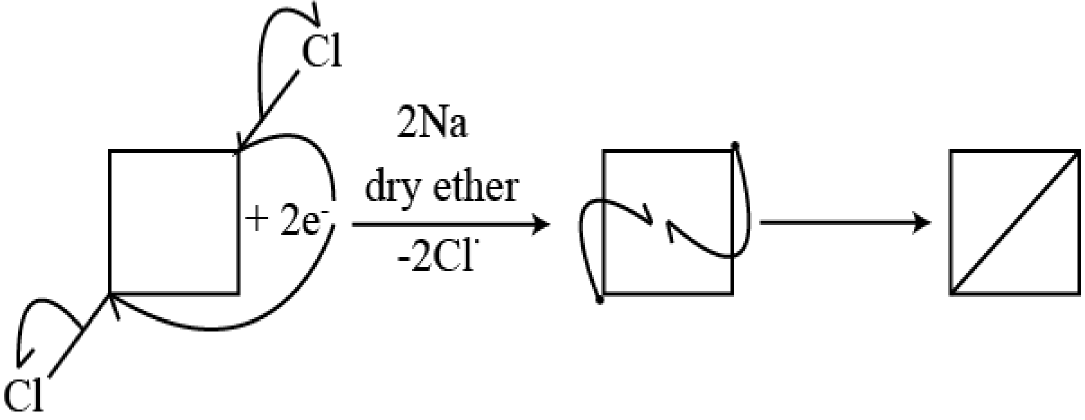
✗ **B.** 

✗ **C.**

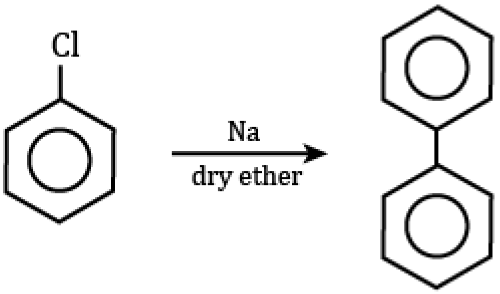


☒ **D.** None of the above

In wurtz reaction, disubstituted cyclic haloalkanes undergo intramolecular cyclization as shown below in the mechanism. Hence the correct option is a.



18. The below reaction is known as :



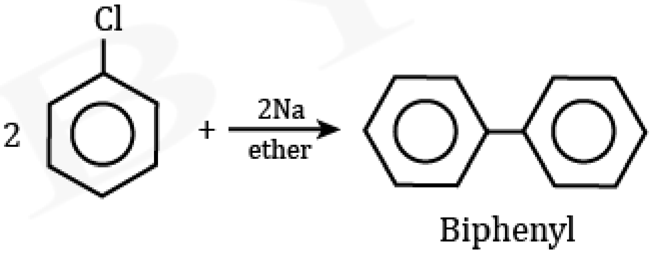
✗ **A.** Wurtz reaction

✗ **B.** Wurtz fittig reaction

✓ **C.** Fittig reaction

✗ **D.** Kolbe's electrolysis

It is the example of fittig reaction in which 2 molecules of aryl halide reacts with 2 mole of Na in presence of ether to form biphenyl.
Fittig reaction follows the similar mechanism as Wurtz reaction.



19. Action of alcoholic $AgNO_3$ on chlorobenezene is similar to the action on

☒ **A.** Ally chloride

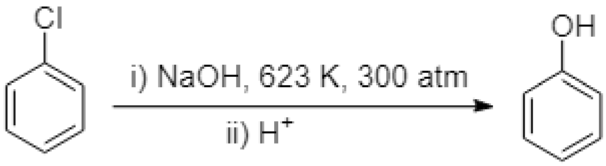
☑ **B.** Vinyl chloride

☒ **C.** Isopropyl chloride

☒ **D.** Benzyl chloride

Both vinyl chloride and chlorobenzene give no precipitate with alcoholic $AgNO_3$ because both have chlorine atoms which are not reactive.
In Chlorobenzene, the chlorine atom is directly attached at the unsaturated carbon atom. In vinyl chloride also, the chlorine atom is directly attached to unsaturated carbon atom.
Hence, the action of alcoholic $AgNO_3$ on chlorobenzene is similar to the action on vinyl chloride. Chlorine atoms are not reactive.

20. Following equation illustrates



☑ **A.** Dow's process

☒ **B.** Kolbe's process

☒ **C.** Carbylamine test

☒ **D.** Haloform reaction

Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of $623\ \mathrm{K}$ and a pressure of $300\ \mathrm{atm}$. This is Dow's process.