



Authentic

SHORTCUTS, TIPS & TRICKS in CHEMISTRY

for JEE MAIN, ADVANCED and KVPY

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Strategic Book for
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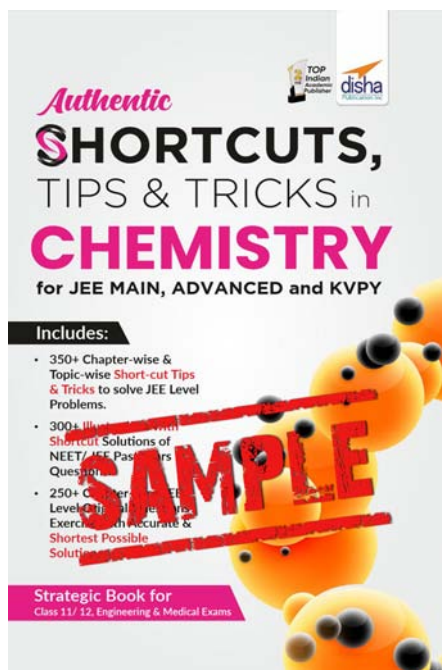
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24. Alcohols, Phenols and Ethers

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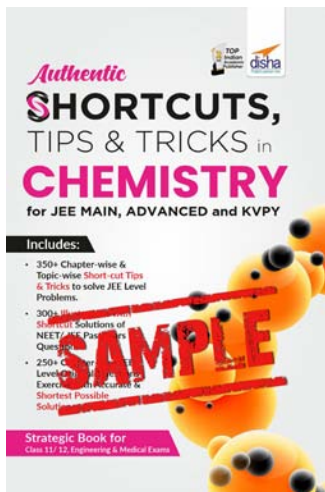
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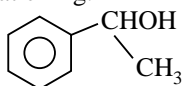
Alcohols, Phenols and Ethers

1

ALCOHOLS

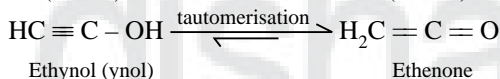
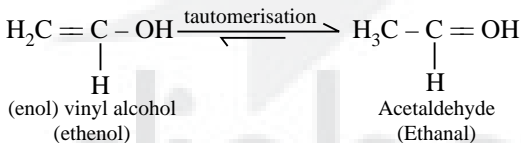
Topic-1 : Classification

- 1.1 Benzylic alcohols are not considered as phenols because the hydroxyl group is not attached to an aromatic ring.

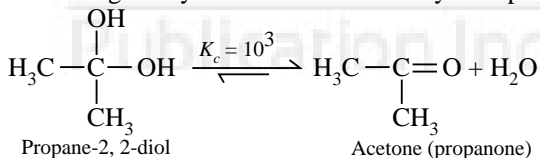


2° benzylic alcohol

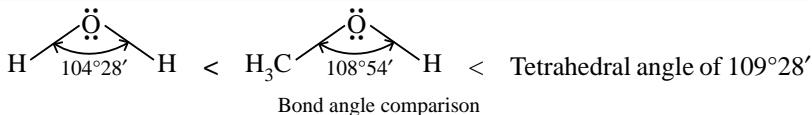
- 1.2 When the hydroxyl group is attached to unsaturated carbon atom (enol or yno), these convert to more stable forms.



- 1.3 Most of the gem diols are unstable because of repulsion between two oxygen atoms. These undergo dehydration to form carbonyl compounds.



Topic-2 : Structure



Topic-3 : Physical Properties

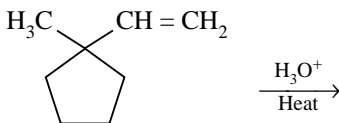
3.1 Boiling point

No. of carbon atoms ↑	B.P. ↑
No. of branches ↑	B.P. ↓
Intermolecular H – bonding ↑	B.P. ↑

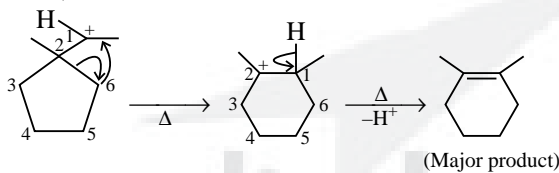
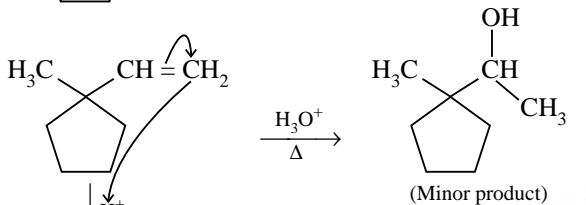
Illustration-2 :

The major product in the following reaction is :

[JEE Main, Sep. 02, 2020 (I), Similar to NEET 2015 RS]



Sol.



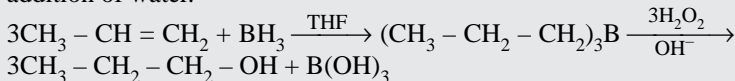
In the presence of heat, the major product will be that alkene which is most substituted.



TIPS AND TRICKS: (T-2)

4.2 Hydroboration - oxidation of alkene

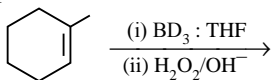
- No formation of intermediate carbocation \Rightarrow anti-Markovnikov addition of water.



- Reaction is stereoselective due to *syn*-addition of $-\text{H}$ and $-\text{OH}$.
- In the formed alcohol, $-\text{H}$ is generated from BH_3/THF and $-\text{OH}$ is from $\text{H}_2\text{O}_2/\text{OH}^-$.

Illustration-3 :

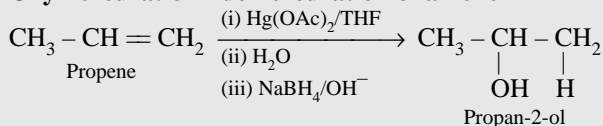
Draw structure of all possible alcohols for the following reaction :





TIPS AND TRICKS: (T-3)

4.3 Oxymercuration - demercuration of alkene

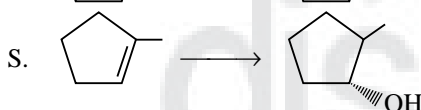
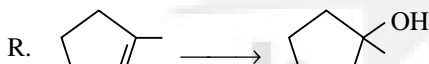


- Regiospecific reaction - Markovnikov addition of water.
- No intermediate carbocation \Rightarrow No rearrangement \Rightarrow Yield of major product is high.
- Stereochemistry is not important when free rotation is possible.
- -OH part comes from H₂O and -H part comes from NaBH₄.

Illustration-6 :

Match the chemical conversion in List-I with the appropriate reagents in List-II. [JEE Adv. 2013]

List-I

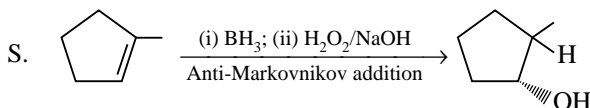
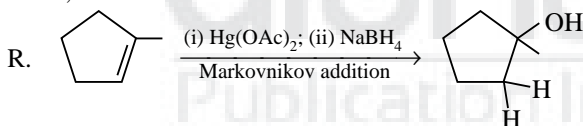


List-II

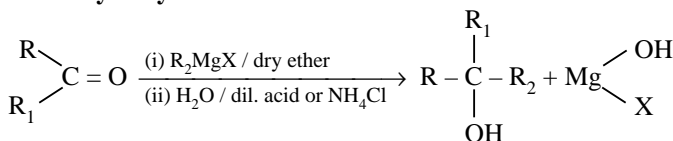
1. (i) Hg(OAc)₂; (ii) NaBH₄

2. (i) BH₃; (ii) H₂O₂/NaOH

Sol. R - 1, S - 2



4.4 Reaction of Grignard reagent with aldehyde and ketone followed by acidic hydrolysis.



Formaldehyde \longrightarrow Primary alcohol

Other aldehyde \longrightarrow Secondary alcohol

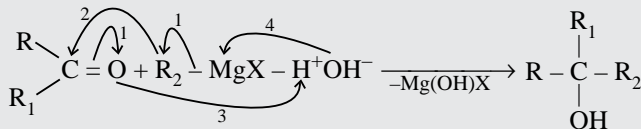
Ketone \longrightarrow Tertiary alcohol



TIPS AND TRICKS: (T-4)

- In the formed alcohol, $-H$ comes from H_2O and the added alkyl group comes from the Grignard reagent.

Mechanism :

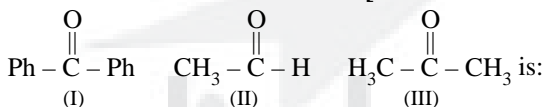


- The reaction of Grignard reagent with carbonyl compound is an example of nucleophilic addition. The ease of reaction will increase with the electron deficiency of carbonyl carbon.

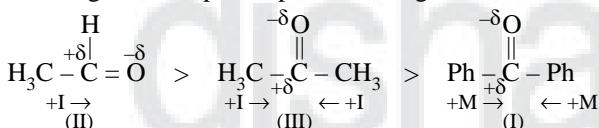
Illustration-7 :

The correct order of reactivity of Ph MgBr with

[JEE 2004 Screening, NEET 2011]

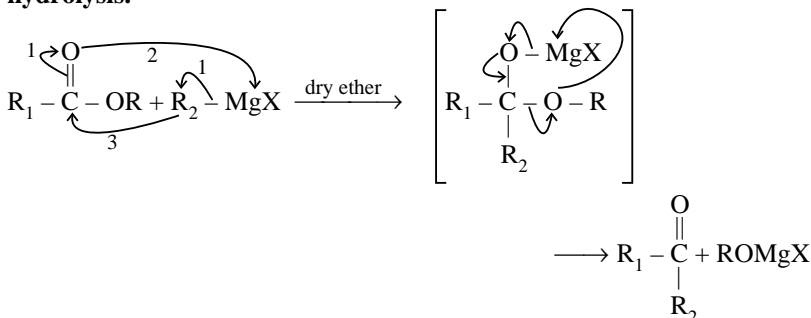


Sol. The magnitude of partial positive charge is in the order:



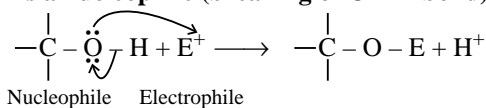
Hence, this is the order of reactivity with Ph MgBr also.

4.5 Reaction of Grignard reagent with acid halide or esters followed by hydrolysis.



When $R_2 - MgX$ is in excess, the formed ketone will react with it and upon hydrolysis, it will produce a tertiary alcohol.

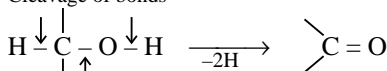
5.2.2 As a nucleophile (breaking of O – H bond) :



Topic-6 : Chemical Reactions

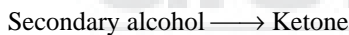
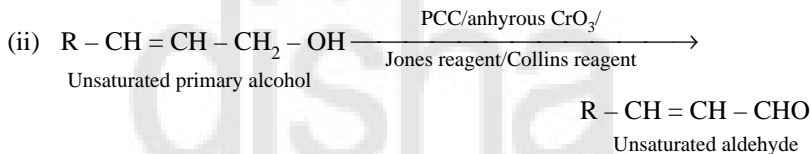
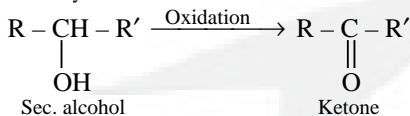
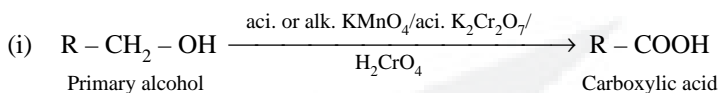
6.1 Oxidation

Cleavage of bonds



formation of bond
Alcohol

Carbonyl compound
(aldehyde, ketone or carboxylic acid)



(iii) With heated copper, primary and secondary alcohols oxidise to produce aldehydes and ketones respectively.

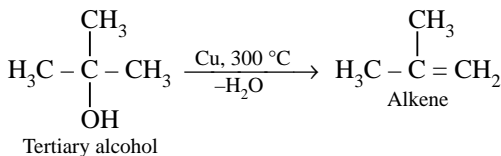
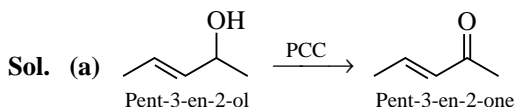


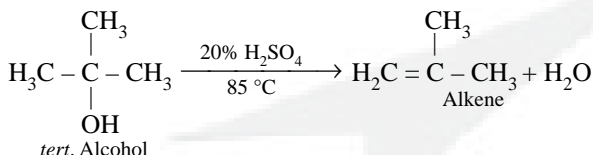
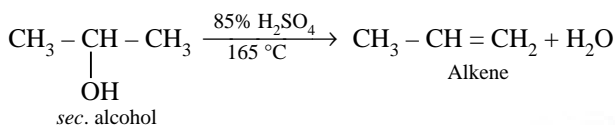
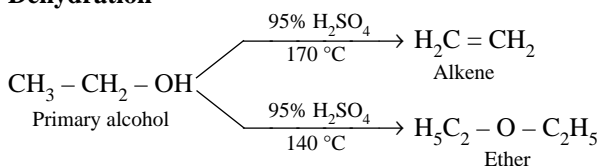
Illustration-9 :

The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is :

- (a) Pyridinium chloro-chromate [JEE 2005]
 (b) Chromic anhydride in glacial acetic acid
 (c) Acidic dichromate
 (d) Acidic permanganate



6.2 Dehydration



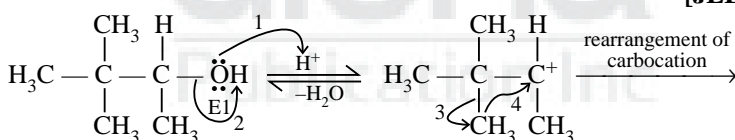
Order of ease of dehydration :

3° alcohol > 2° alcohol > 1° alcohol

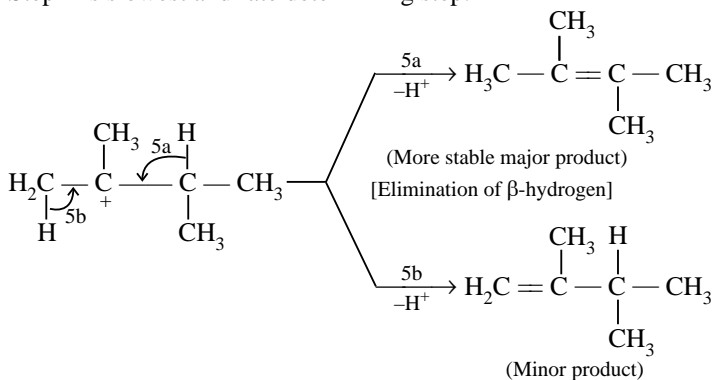
Mechanism :

Mechanism of dehydration of a secondary alcohol (3, 3-dimethylbutan-2-ol):

[JEE 1996]



Step 2 is slowest and rate determining step.





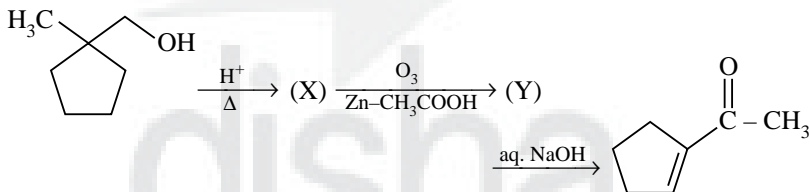
TIPS AND TRICKS: (T-6)

- The ease of dehydration of alcohol increases with the stability of initial formed intermediate carbocation.
- For 2° and 3° alcohol, step 2 and 5 \Rightarrow E1 mechanism.
- For 1° alcohol, removal of water and β -hydrogen occur in a single step \Rightarrow E2 mechanism.
- Determination of major alkene \Rightarrow Zaitsev's rule.
- Using hydrohalic acid (HCl, HBr, HI) instead of $H_2SO_4/H_3PO_4 \Rightarrow$ Formation of alkyl halide.
- If no $\beta - H$ is present in the intermediate carbocation, primary alcohol would follow E1 mechanism.

Illustration-10 :

Identify (X) and (Y) in the following reaction sequence.

[JEE 2005, Similar to JEE Main Sep. 04, 2020 (I)]



Sol. We can identify (X) by the major product formed upon acid catalysed dehydration of the given primary alcohol.

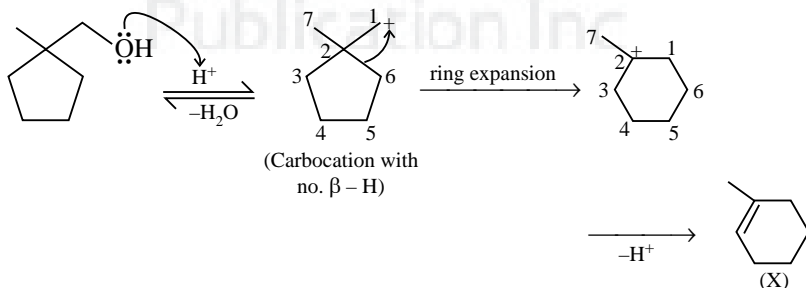
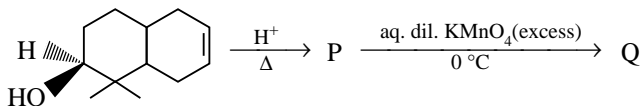


Illustration-11 :

The number of hydroxyl group(s) in Q is :

[JEE Adv. 2015]



Sol. (4)

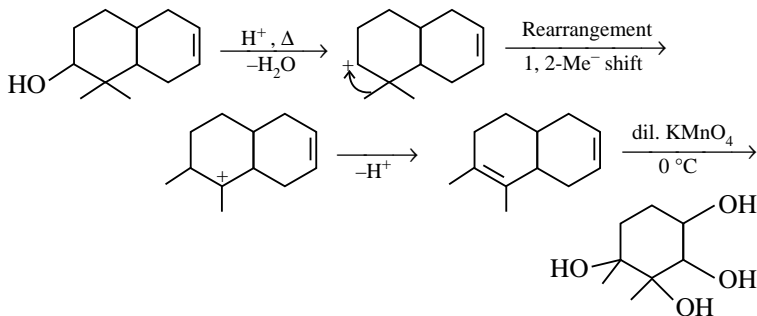
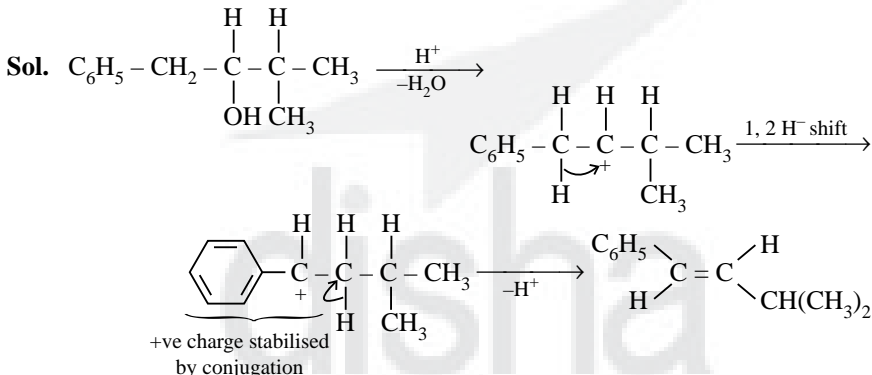


Illustration-12 :

The main product of the following reaction is :

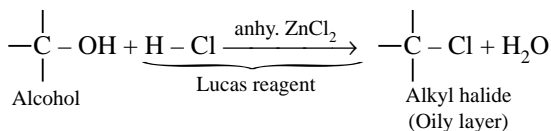
[JEE 2010]



trans-isomer (major product) is more stable than *cis*-isomer (minor product).

Topic-7 : Differentiation between Primary, Secondary and Tertiary Alcohols

7.1 Lucas Test



Primary alcohol \Rightarrow Formation of oily layer only after heating

Secondary alcohol \Rightarrow Formation of oily layer within 5 min.

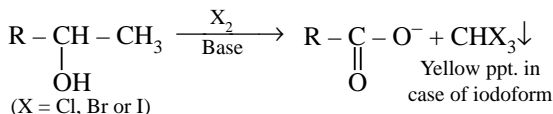
Tertiary alcohol \Rightarrow Formation of oily layer immediately.



TIPS AND TRICKS: (T-7)

- The mechanism (S_N1) involves formation of carbocation intermediate. Thus, tertiary, allyl and benzyl alcohols give this test immediately.
- Low molecular mass (up to 5 carbons) alcohols are soluble in Lucas reagent but alkyl halides are not.

7.2 Haloform Reaction



TIPS AND TRICKS: (T-8)

- Only ethanol and alcohols having $-\text{CH}(\text{OH})-\text{CH}_3$ group give positive haloform reaction.

Illustration-13 :

Among the following, the one that gives positive iodoform test upon reaction with I_2 and NaOH is : [JEE 2006]

- (a) $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \text{CH}_2\text{OH}$ (b) $\text{Ph} - \text{CH}(\text{OH}) - \text{CH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$

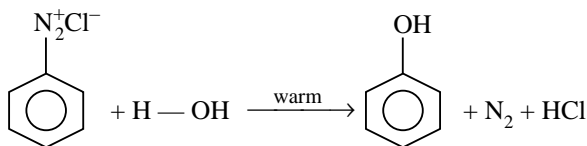
Sol. (b) $-\text{CH}(\text{OH})\text{CH}_3$ group is present only in option (b); which can give positive iodoform test.

PHENOLS

Topic-1: Preparation

1.1 Laboratory Preparation

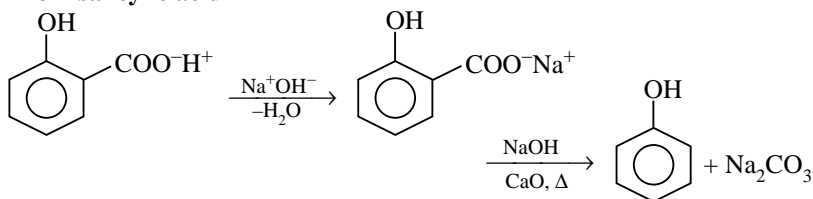
1.1.1 From diazonium salts



TIPS AND TRICKS: (T-9)

- In alkaline solution, phenol can couple with the remaining diazonium salt to form azo compounds.
- The rate of coupling reaction can be reduced by making the solution highly acidic. This can be achieved by adding the diazonium solution slowly to boiling dilute sulphuric acid.

1.1.2 From salicylic acid



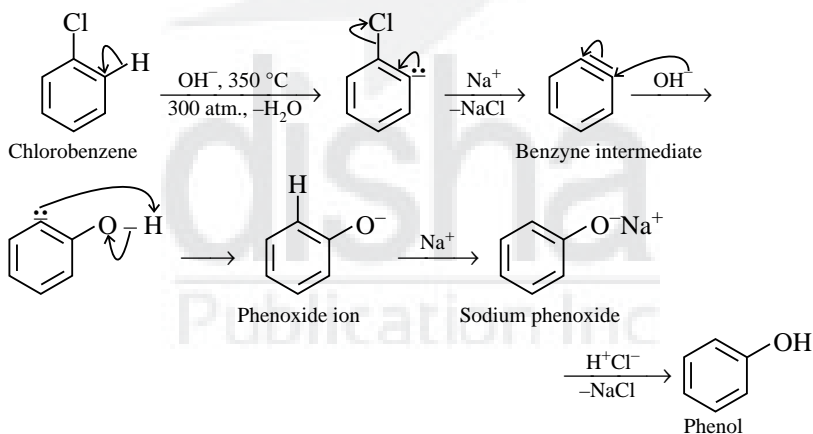
TIPS AND TRICKS: (T-10)

- Use of soda lime (NaOH + CaO) is recommended instead of NaOH because soda lime has much less tendency to absorb atm. water.

1.2 Industrial Preparation

1.2.1 From haloarene (Dow process)

First chlorobenzene is fused with NaOH to get sodium phenoxide which upon acidification produces phenol.



1.2.2 From benzenesulphonic acid

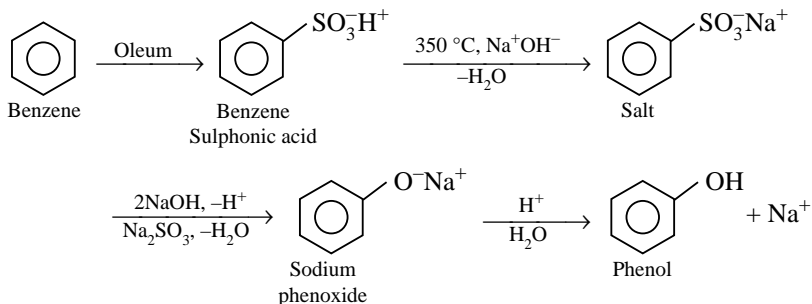
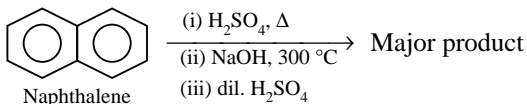
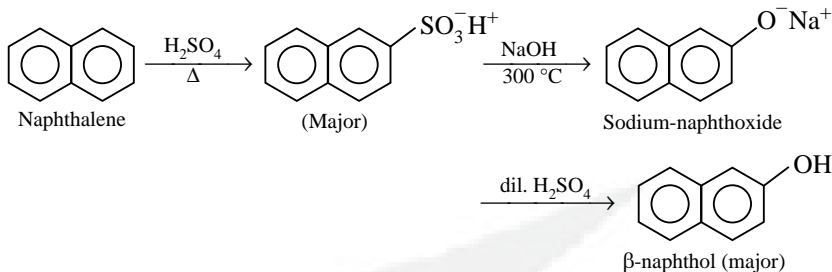


Illustration-14:

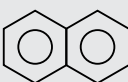
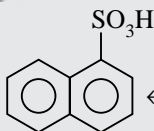
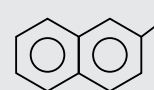
Write the major product of the following reaction.



Sol.

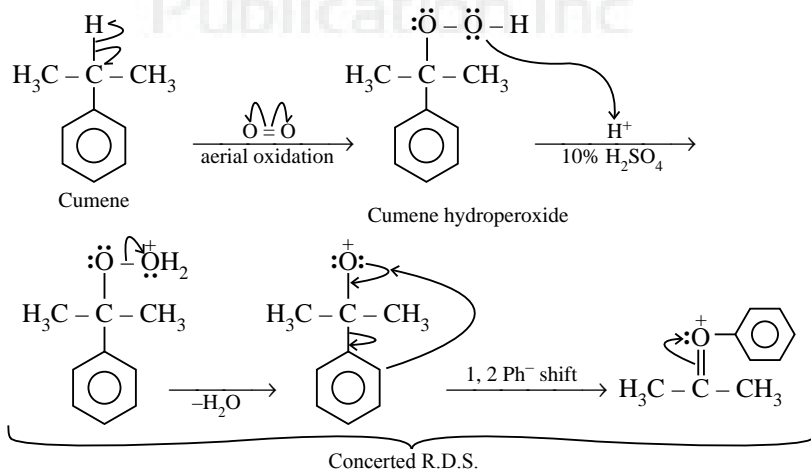


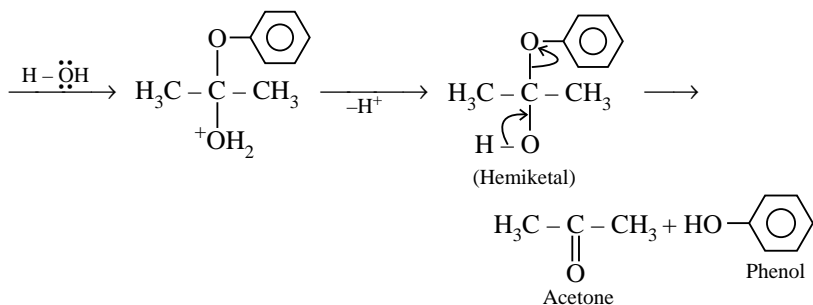
TIPS AND TRICKS: (T-11)


 $\xrightarrow[80\text{ }^\circ\text{C}]{\text{H}_2\text{SO}_4}$

 $\xrightarrow[165\text{ }^\circ\text{C}]{\text{H}_2\text{SO}_4}$


Kinetically favoured product Naphthalene Thermodynamically favoured product

1.2.3 From cumene





TIPS AND TRICKS: (T-12)

- An aryl group has greater migratory aptitude than an alkyl group for 1, 2-shift. See the concerted R.D.S.

Topic-2 : Chemical Properties

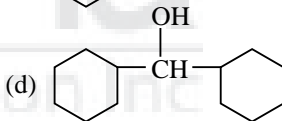
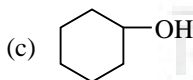
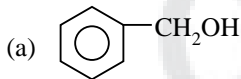
2.1 Acidic Nature of Phenol

Carboxylic acid > Phenol > Water > Alcohol

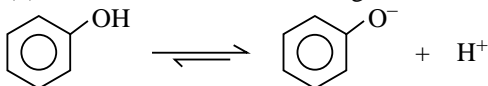
$$K_a : \quad \approx 10^{-5} \quad \approx 10^{-10} \quad 10^{-14} \quad \approx 10^{-16}$$

Illustration-15 :

Which one of the following compounds has the most acidic nature?



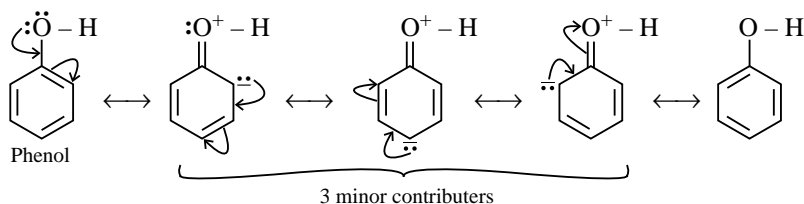
Sol. (b) Phenols are 10^6 times stronger acid than alcohols.

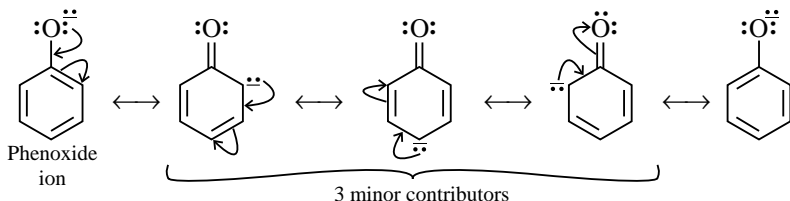


Phenol

Phenoxide ion

- Both phenol and phenoxide ion are resonance stabilized. But phenoxide ion must be more stable. Let's see :





If we compare the minor contributors of phenol and phenoxide ion, we can see that due to +ve and -ve charge separation in phenol, it is less resonance stabilized than phenoxide ion.

Illustration-16 :

The ionization constant of phenol is higher than that of ethanol because :

- Phenoxide ion is bulkier than ethoxide
- Phenoxide ion is stronger base than ethoxide
- Phenoxide ion is stabilized through delocalization
- Phenoxide ion is less stable than ethoxide

Sol. (c) There is no delocalization of negative charge in ethanol.



TIPS AND TRICKS: (T-13)

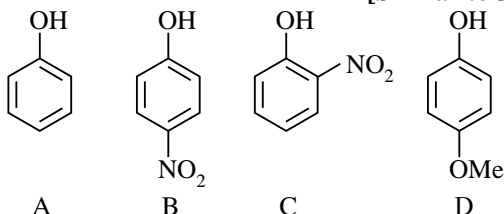
Effect of substituent on acidic nature:

- The substituents showing -M or -I effect decreases the negative charge of phenoxide ion and thus, increase the acidic characters. This effect is more pronounced at ortho and para positions.
- The substituents showing +M or +I effect decreases the acidic character (more at ortho and para positions).

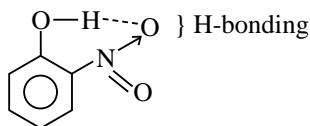
Illustration-17 :

The increasing order of pK_a values of the following compounds is :

[Similar to JEE Main, Jan 10, 2019 (I)]



Sol. Due to -M effect of $-\text{NO}_2$ it will increase the acidic nature. Due to +M effect of $-\text{OCH}_3$, it will decrease the acidic nature. There is intramolecular H-bonding in *o*-nitrophenol. This will decrease the proton donating nature. Thus, its acidity will be less than *p*-isomer.



Correct order of acidity : $B > C > A > D$

Correct order of pK_a : $B < C < A < D$

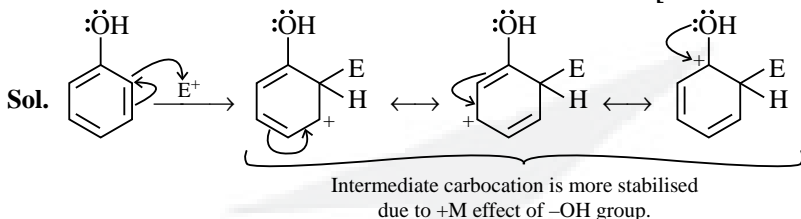
2.2 Chemical Reactivity

Due to +M effect of $-OH$ group, e^- density increases in the ring. This increases its reactivity towards electrophilic aromatic substitution. Moreover, e^- density increases more at o - and p -positions (see the resonating structures).

Illustration-18 :

Statement -1: Phenol is more reactive than benzene towards electrophilic substitution reactions.

Statement-2: In the case of phenol, the intermediate carbocation is more resonance stabilized. [JEE Main 2000 S]



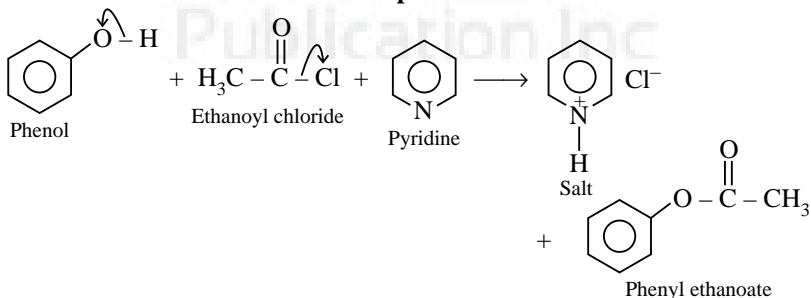
Statement-1 and statement-2 are correct, and statement-2 is the correct explanation of the statement-1.

Topic-3 : Chemical Reactions

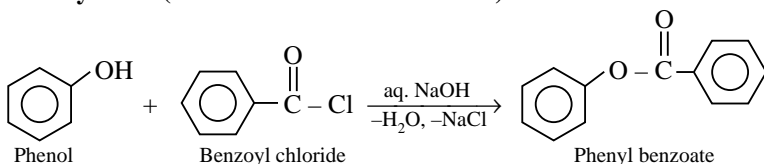
3.1 Esterification : Formation of phenyl esters

Phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

3.1.1 Reaction with acid chloride in the presence of a base

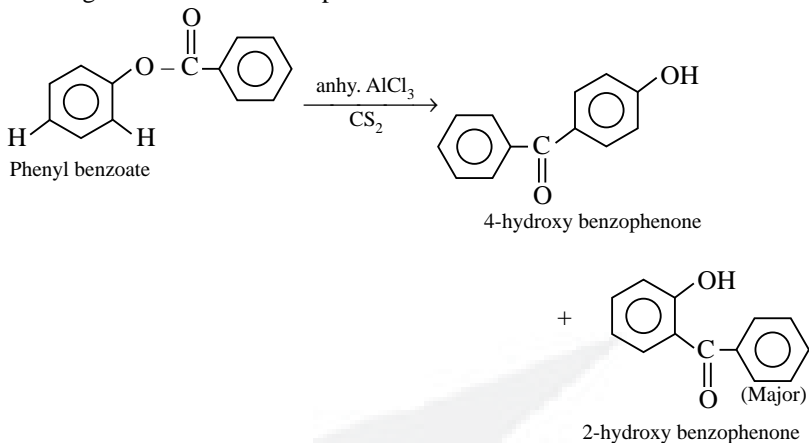


3.1.2 Benzoylation (Schotten Baumann Reaction)



3.1.3 Fries rearrangement

When phenyl esters are treated with anhydrous AlCl_3 in CS_2 solvent, a rearrangement reaction takes place.



3.2 Electrophilic Aromatic Substitution Reactions

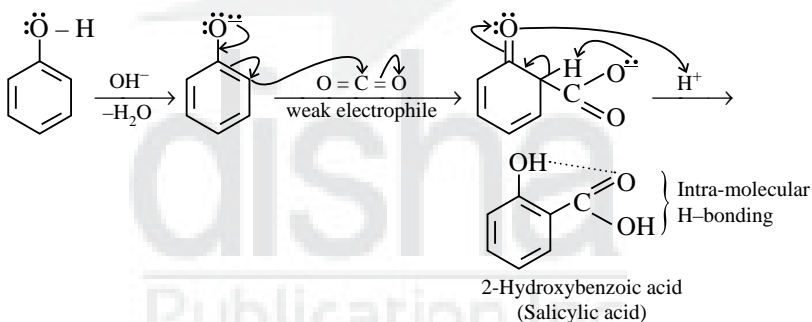
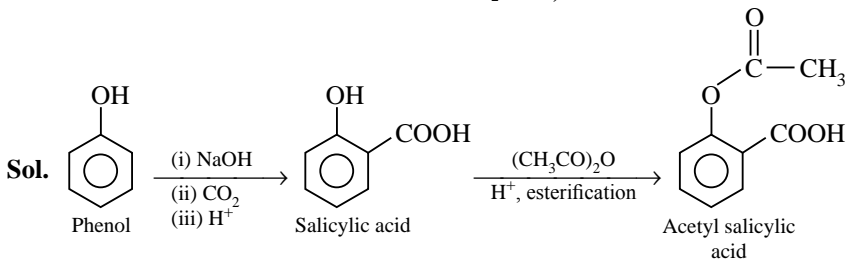


Illustration-19 :

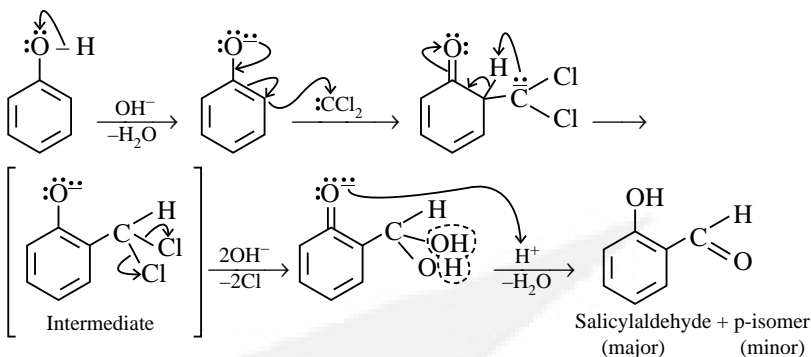
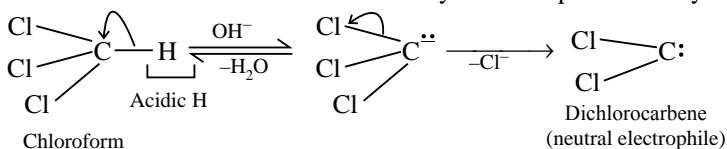
Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with $(\text{CH}_3\text{CO})_2\text{O}$ in the presence of catalytic amount of H_2SO_4 produces :

[2018, Similar to JEE Main 2014]



3.2.2 Reimer-Tiemann Reaction

Phenol react with chloroform and sodium hydroxide to produce salicylaldehyde.



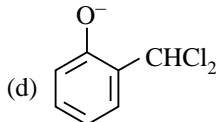
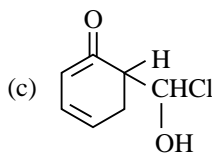
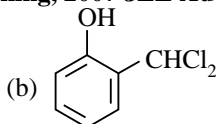
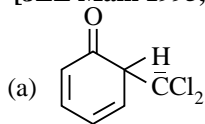
TIPS AND TRICKS: (T-14)

- The electrophile $:CCl_2$ attacks at C^{\ominus} not $:O^{\ominus}$ because C^{\ominus} is a better nucleophile than O^{\ominus} .
- $:CCl_2$ attacks at ortho position (majorly) because there is intra-molecular H-bonding in the final product.

Illustration-20 :

When phenol is reacted with $CHCl_3$ and $NaOH$ followed by acidification, salicylaldehyde is obtained. Following species are involved in the above mentioned reaction as intermediates?

[JEE Main 1995, Similar to 1995 Screening, 2007 JEE Adv. (Passage)]

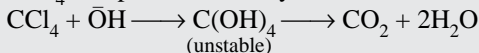


Sol. (a) and (d)



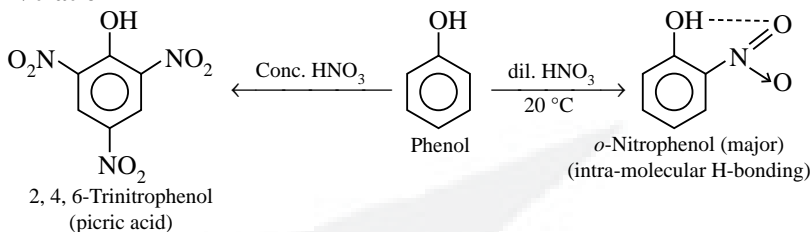
TIPS AND TRICKS: (T-15)

- With CH_2Cl_2 , the reaction rate is low due to less acidic hydrogens in it.
- With CCl_4 , the product is salicylic acid.



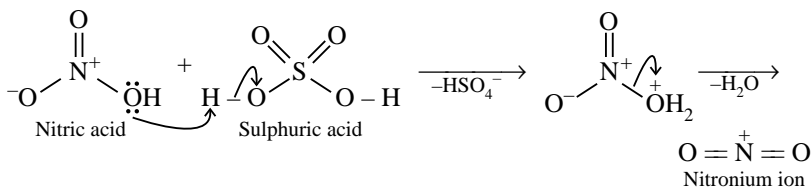
Now, CO_2 reacts with phenol and the rest of the mechanism is same as Kolbe's reaction.

3.2.3 Nitration

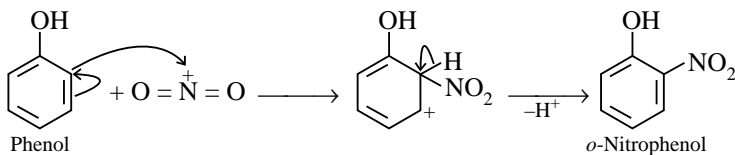


TIPS AND TRICKS: (T-16)

- The electrophile is nitronium ion NO_2^+ . To generate NO_2^+ easily or to increase the rate of reaction, dil. H_2SO_4 is used.



By Le Chatelier's principle, H_2SO_4 shifts the equilibrium to make more NO_2^+ .

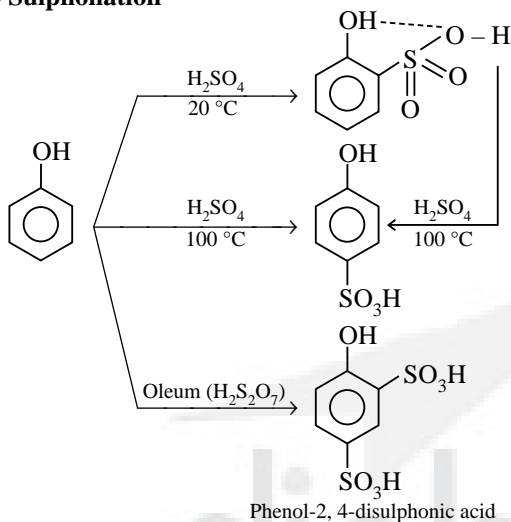




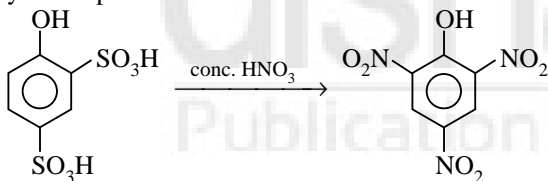
TIPS AND TRICKS: (T-17)

- The yield of picric acid is low by this method. This is due to the fact that $-\text{NO}_2$ is an e^- withdrawing group which deactivates the ring for further nitration.

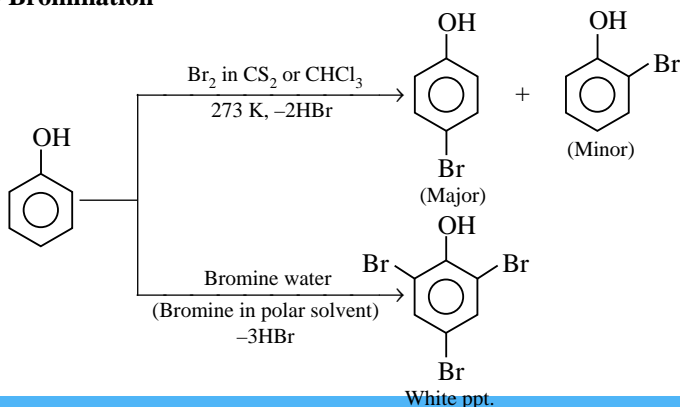
3.2.4 Sulphonation



Reaction of phenol-2, 4-disulphonic acid with conc. HNO_3 gives a good yield of picric acid.



3.2.5 Bromination

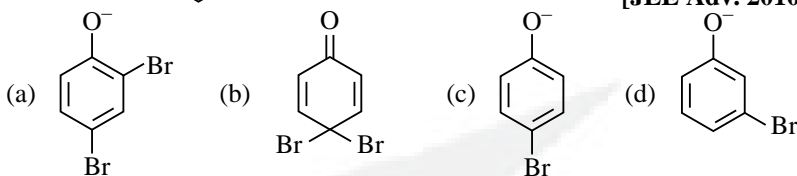
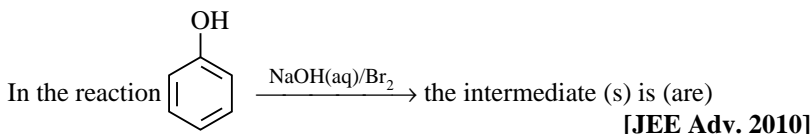




TIPS AND TRICKS: (T-18)

- The electrophile in this reaction is brominium ion (Br^+). In case of phenols, the polarisation of bromine molecule takes place even in the absence of Lewis acid (FeBr_3) due to highly activating $-\text{OH}$ group.

Illustration-21:



Sol. (a) and (c)

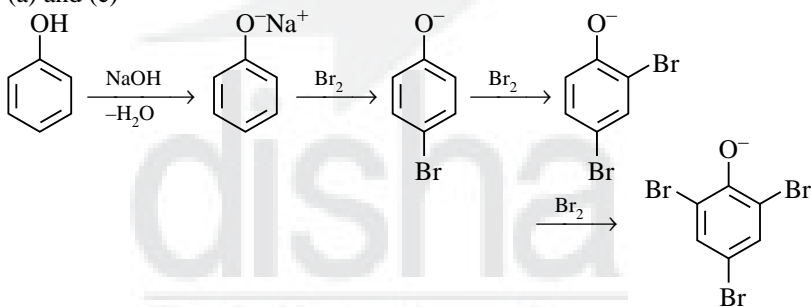
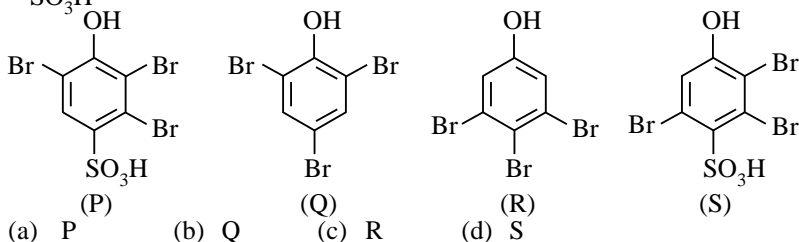
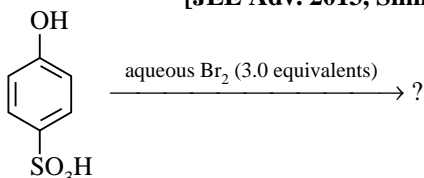


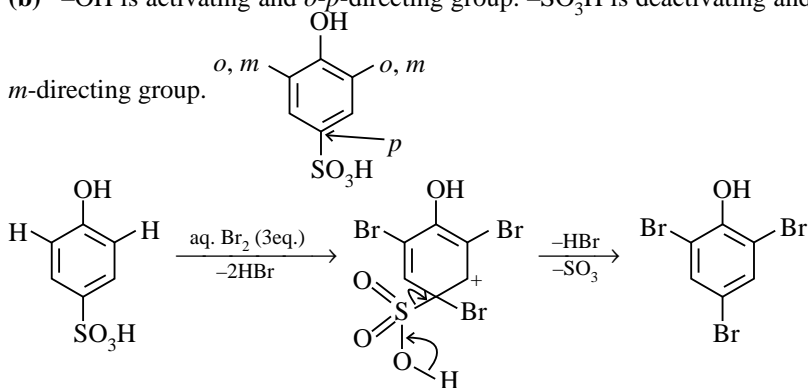
Illustration-22 :

The major product(s) of the following reaction is(are)

[JEE Adv. 2013, Similar to JEE Main Jan. 11, 2019 (I)]



Sol. (b) $-\text{OH}$ is activating and o - p -directing group. $-\text{SO}_3\text{H}$ is deactivating and



TIPS AND TRICKS: (T-19)

- Ipsso substitution is possible because $-\text{SO}_3\text{H}$ is a very good leaving group.

ETHERS

Topic-1 : Structure

C - O bond length : Aliphatic Ether \approx Alcohol $>$ Phenol.

Due to partial double bond character in phenol, it has minimum bond length. C - O - C bond angle in ether is more than the tetrahedral angle due to repulsive interaction between two bulky ($-\text{R}$) groups.

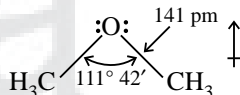
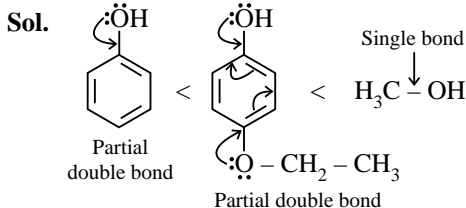


Illustration-23 :

Arrange the following compounds in increasing order of C - OH bond length: methanol, phenol, p -ethoxyphenol [JEE Main, Jan. 08, 2020 (I)]

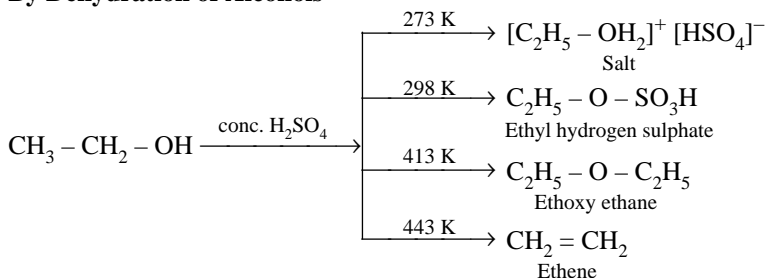


TIPS AND TRICKS: (T-20)

- Due to competing resonance in p -ethoxyphenol, the double bond character in C - OH bond is less than that in phenol.

Topic-2 : Preparation

2.1 By Dehydration of Alcohols



Mechanism:

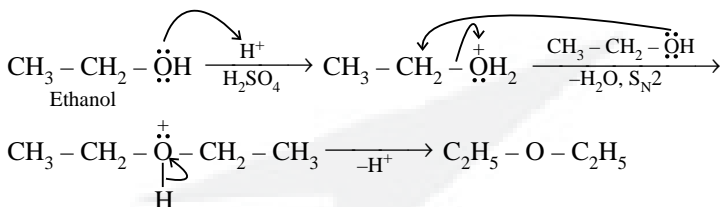


Illustration-24 :

Consider the following reaction :



Among the following, which one cannot be formed as a product under any conditions ?

[JEE Main, 2011RS]

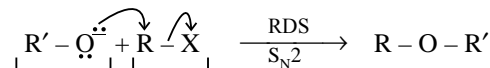
- (a) Ethylene (b) Acetylene
(c) Diethyl ether (d) Ethylhydrogen sulphate

Sol. (b) Acetylene cannot be prepared under any condition.

2.2 Williamson Synthesis



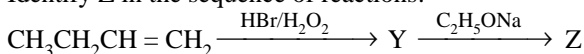
Mechanism:



Can be any 1° alkyl halide
alkoxide ion for low steric
(1°, 2° or 3° hindrance)

Illustration-25 :

Identify Z in the sequence of reactions:



[NEET 2014, Similar to JEE Main 2014]

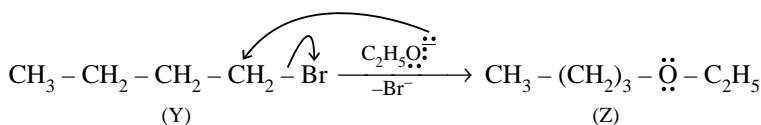
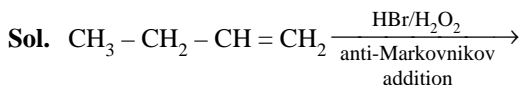
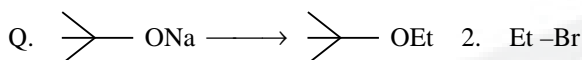
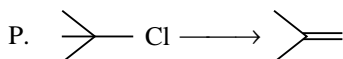


Illustration-26 :

Match the chemical conversions in List-I with the appropriate reagents in List-II. [JEE Adv. 2013, Similar to JEE M April 22, 2013]

List-I

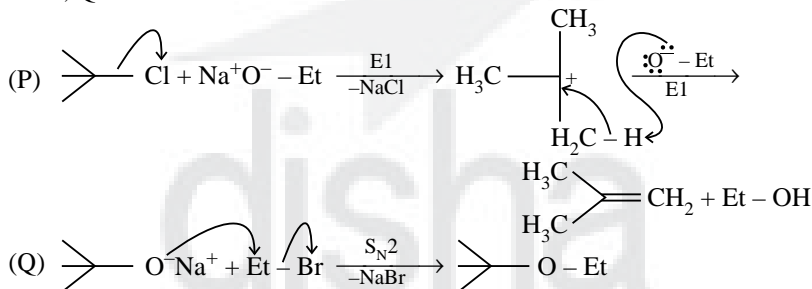


List-II

1. NaOEt

2. Et-Br

Sol. P - 1, Q - 2



TIPS AND TRICKS: (T-21)

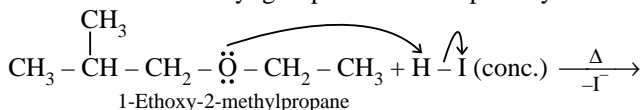
- In case of tertiary alkyl halide, instead of substitution, elimination occurs. For secondary alkyl halide, elimination competes with substitution. Aryl ethers can also be prepared by this method by using derivatives of phenol and a primary alkyl halide.

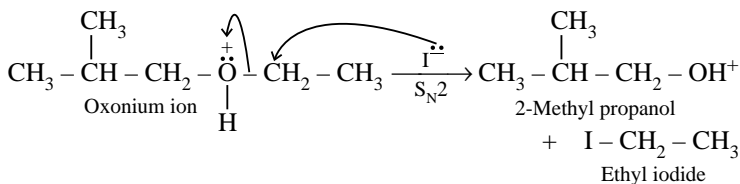
Topic-3 : Chemical Reactions

3.1 Reaction with H - X (cleavage of C - O bond)

3.1.1 When hydrogen halides are not in excess

Case-I : Both the alkyl groups of ether are primary or secondary.





[NEET 2007, Similar to JEE Main Sep. 04, 2020 (II), NEET 2006]

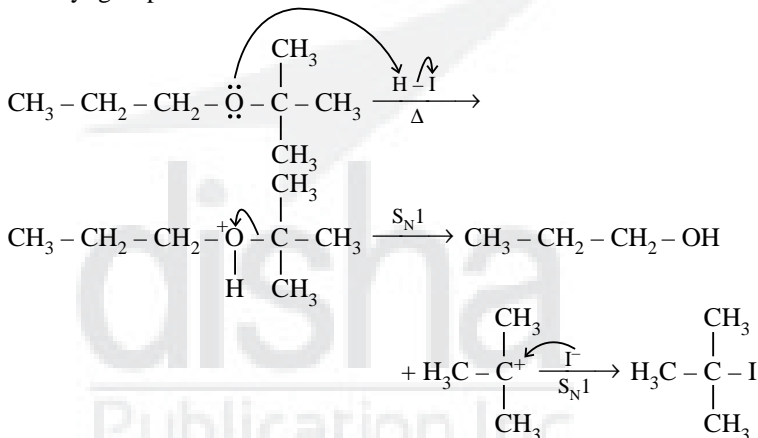


TIPS AND TRICKS: (T-22)

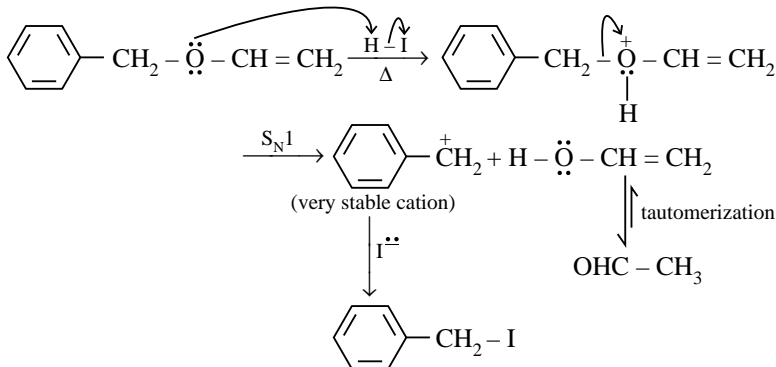
- Due to less steric hindrance, attack of I^- (nucleophile) takes place at lower alkyl group.

Case-II : When one of the alkyl group is tertiary or benzyl or allyl.

(i) 3° alkyl group



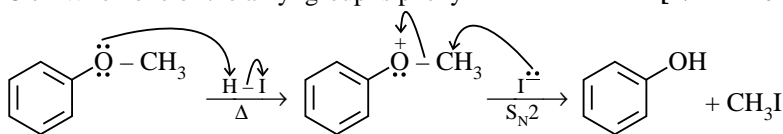
(ii) Benzyl group ($\text{Ph} - \text{CH}_2$)



[JEE Main Sep. 02, 2020 (II)]

Case-3 : When one of the alkyl group is phenyl

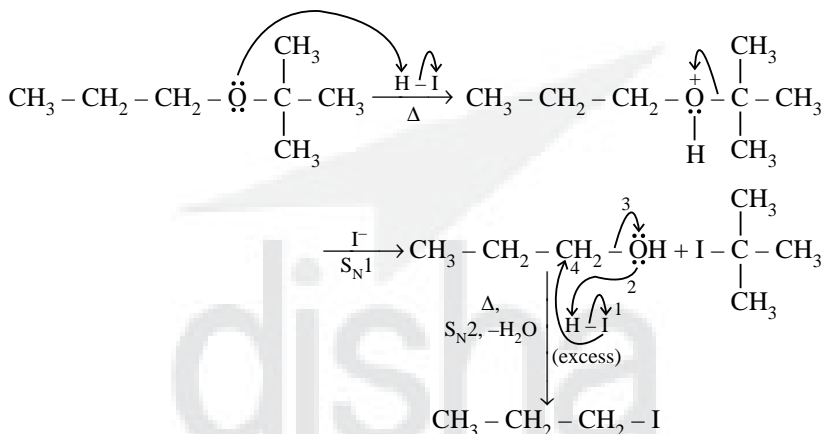
[NEET 2020]



TIPS AND TRICKS: (T-23)

- Aryl-oxygen bond is more stable than alkyl-oxygen bond. Thus, aryl ethers always yield phenol as one of the product.

3.1.2 When hydrogen halides are in excess



[NEET Odisha 2019; Similar to JEE M Online April 9, 2013]



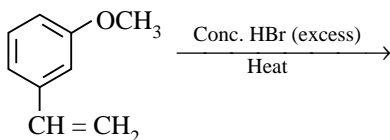
TIPS AND TRICKS: (T-24)

- In the presence of excess H – I, the formed alcohol would further react with acid to form alkyl halide. Phenol (or derivatives of it) will not undergo this change.

Illustration-27 :

The major product of the following reaction is :

[JEE Main April 8, 2019 (I), Similar to JEE Main Jan. 12, 2019 (II)]



Sol.

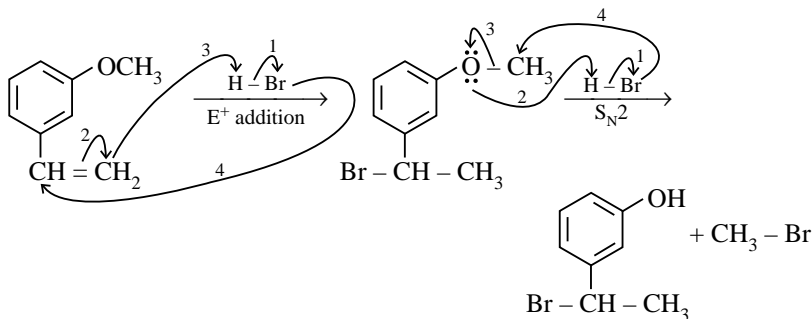
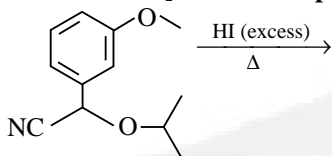


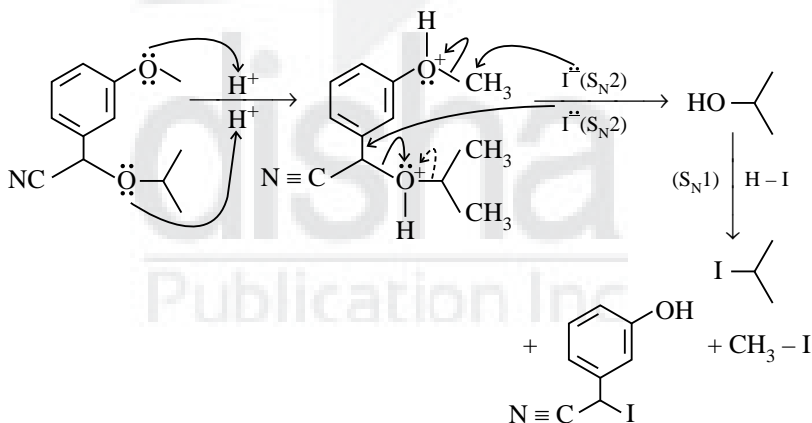
Illustration-28 :

The major product of the following reaction is:

[JEE Main April 10, 2019 (I), Similar to JEE Main 2018]



Sol.

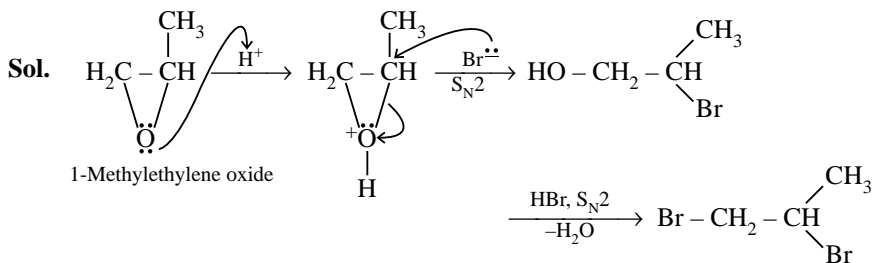


-CN is an electron withdrawing group. There are two possibilities of cleavage of C-O bond (solid curved arrow and dotted arrow). S_N1 mechanism : (i) Either

the formed carbocation can be 2° or (ii) $NC-CH_2^+$; both are not very stable. S_N2 mechanism : -CN will increase the positive charge on bonded carbon, which in turn, facilitates the attack of nucleophile (I^-) and cleavage of C-O bond.

Illustration-29 :

1-Methylethylene oxide when treated with an excess of HBr produces:

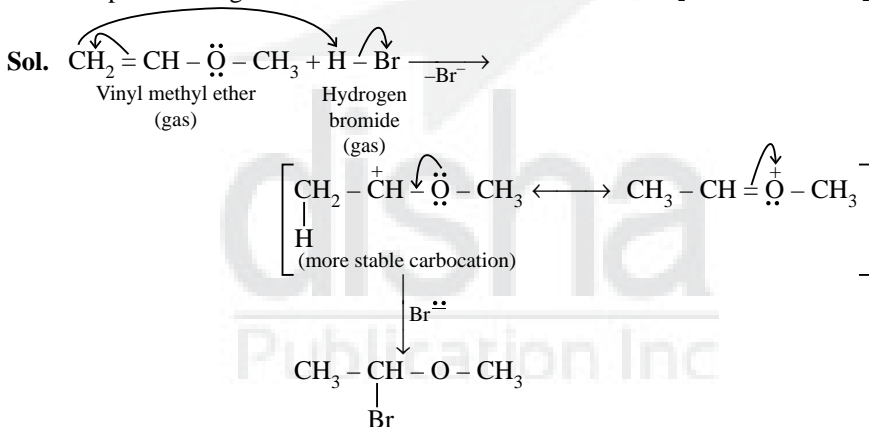


TIPS AND TRICKS: (T-25)

- Acid catalysed ring opening of epoxides through nucleophilic attack occur at a more substituted carbon atom.

Illustration-30 :

HBr reacts with $\text{CH}_2 = \text{CH} - \text{OCH}_3$ under anhydrous conditions at room temperature to give: [JEE Main 2006]



HBr is not in excess and the condition is anhydrous (gas phase), thus, reaction will not proceed further at room temperature.



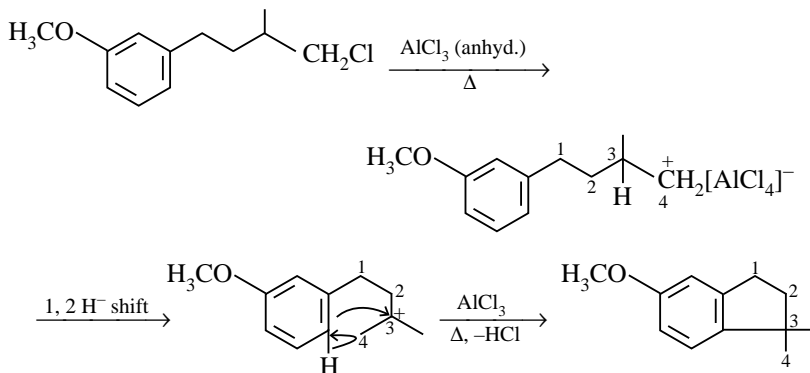
TIPS AND TRICKS: (T-26)

- π cloud is more apt to attack by the proton than the lone pair with oxygen atom.

3.2 Electrophilic Substitution Reactions of Aryl Ethers

3.2.1 Bromination, nitration etc. are similar to phenol. The H-bonding factor will not play a role to decide the major product.

3.2.2 Friedel-Crafts Reactions

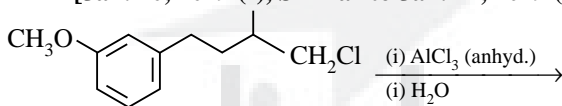


This is an example of intra-molecular Friedel-Crafts alkylation.

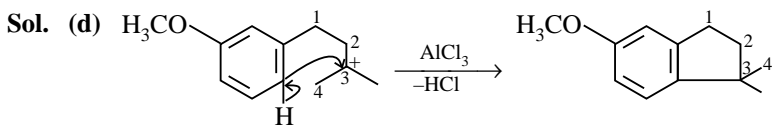
Illustration-31 :

The major product of the following reaction is:

[Jan. 10, 2019 (I), Similar to Jan. 12, 2019 (I), April 10, 2019 (II)]



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



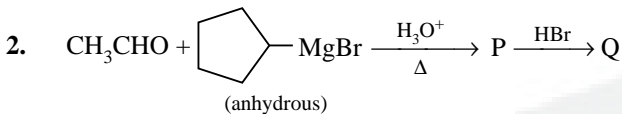


Concept Booster Exercise

Only One Correct Answer

1. Which of the following represents correct increasing order of acid catalysed dehydration of alcohols?

- (i) 1-phenylbutan-1-ol (ii) 1-phenylbutan-2-ol
 (iii) 2-phenylbutan-1-ol (iv) 2-phenylbutan-2-ol
 (a) (iv) = (iii) < (i) = (ii) (b) (i) = (ii) < (iii) = (iv)
 (c) (iii) < (ii) < (i) < (iv) (d) (i) < (ii) < (iv) < (iii)



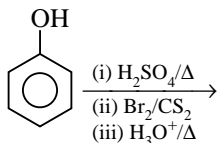
Compound Q obtained from the above reaction is :

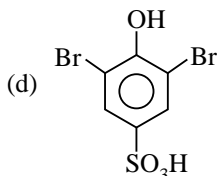
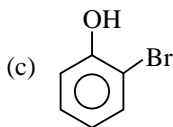
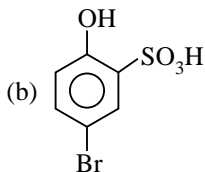
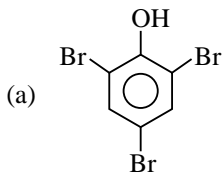
- (a) (b)
 (c) (d)

3. What is the major product upon reaction of catechol, sodium hydroxide and diiodomethane?

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

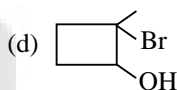
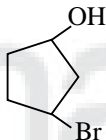
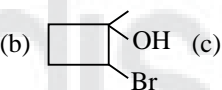
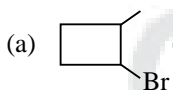
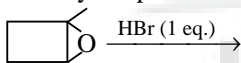
4. Identify the final major product from the following series of reactions:





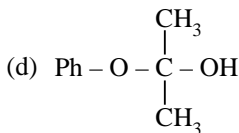
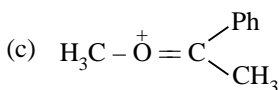
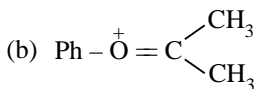
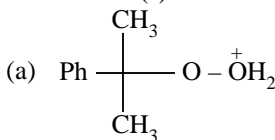
5. Which of the following methods is not suitable to prepare *tert*-butyl ethyl ether?
- (a) *tert*-butyl bromide with sodium ethoxide
 (b) *tert*-butanol with ethanol in acidic condition
 (c) isobutene with ethanol in acidic condition
 (d) sodium *tert*-butoxide with ethyl bromide

6. Identify the product :

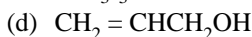
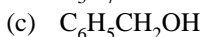
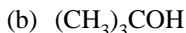
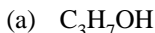


One or More Than One Correct Answer

7. Cumene on reacting with aerial oxygen and then with dil. H_2SO_4 , is converted to phenol and an organic compound. Which of the following is/are reaction intermediate(s)?

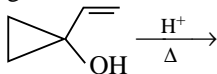


8. Which of the below mentioned compound(s) would react with Lucas reagent at room temperature?

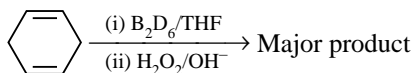


Numerical Answer/Integer Value Answer

9. How many primary hydrogen atoms are present in the major product of the given reaction?

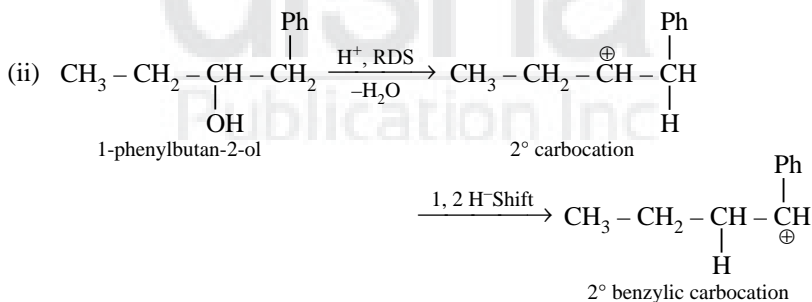
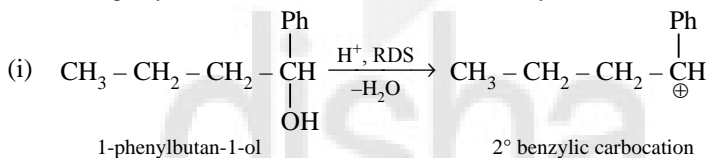
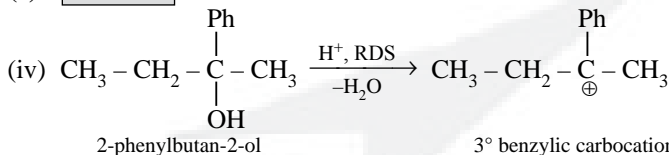


10. Find the total number of isomeric alcohols from the below scheme of reactions:

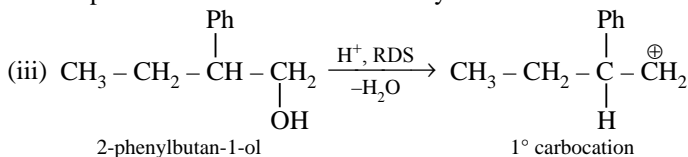


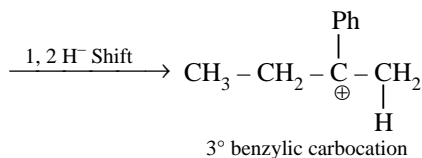
Solutions

1. (c) Using T-6



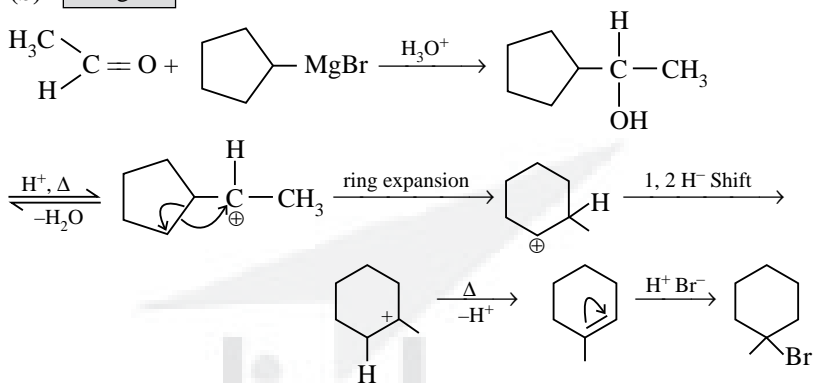
Though 2° benzylic carbocation forms after rearrangement, but this step will not decide the case of dehydration.





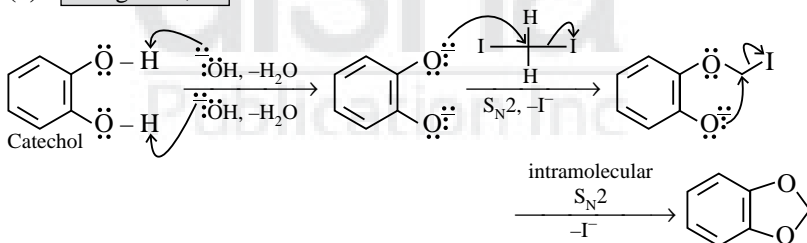
Though 3° benzylic carbocation will be formed after rearrangement, but this step will not decide the rate of dehydration. Hence, the increasing order of ease of dehydration is: (iii) < (ii) < (i) < (iv).

2. (b) Using T-4



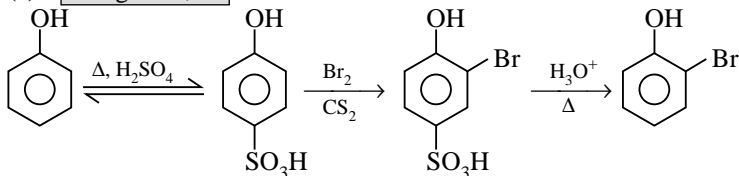
Due to high temp., formed secondary alcohol is susceptible to acid catalysed dehydration.

3. (a) Using T-14, 15

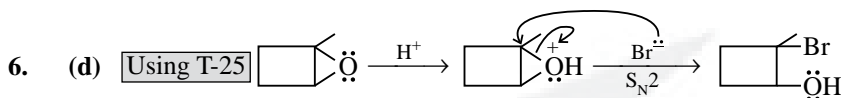


Due to less acidic H in CH₂I₂, the substitution reaction is faster than formation of carbene species.

4. (c) Using T-18, 19

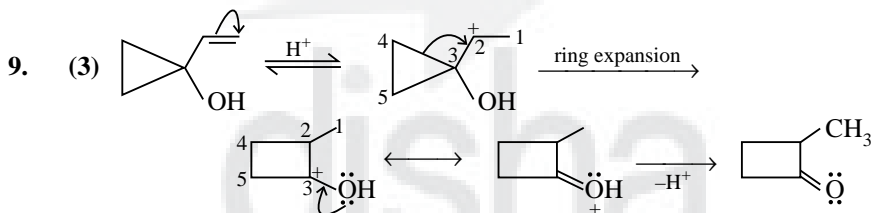


5. (a)
$$\text{H}_3\text{C}-\underset{\text{Br}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3 + \text{C}_2\text{H}_5\text{O}^- \xrightarrow{\text{E2}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$$
- (b)
$$(\text{CH}_3)_3\text{C}-\overset{\text{H}^+}{\text{O}}\text{H} \rightarrow (\text{CH}_3)_3\text{C}-\overset{+}{\text{O}}\text{H}_2 \xrightarrow[\text{-(H}_2\text{O, S}_{\text{N}}2, \text{-H}^+)]{\text{CH}_3-\text{CH}_2-\overset{\text{H}}{\text{O}}\text{H}} (\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_3$$
- (c)
$$(\text{CH}_3)_2\text{C}=\text{CH}_2 \xrightarrow{\text{H}^+} (\text{CH}_3)_2\overset{+}{\text{C}}-\text{CH}_3 \xrightarrow[\text{-H}^+]{\text{CH}_3-\text{CH}_2-\overset{\text{H}}{\text{O}}\text{H}} (\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_3$$
- (d) Williamson synthesis reaction.

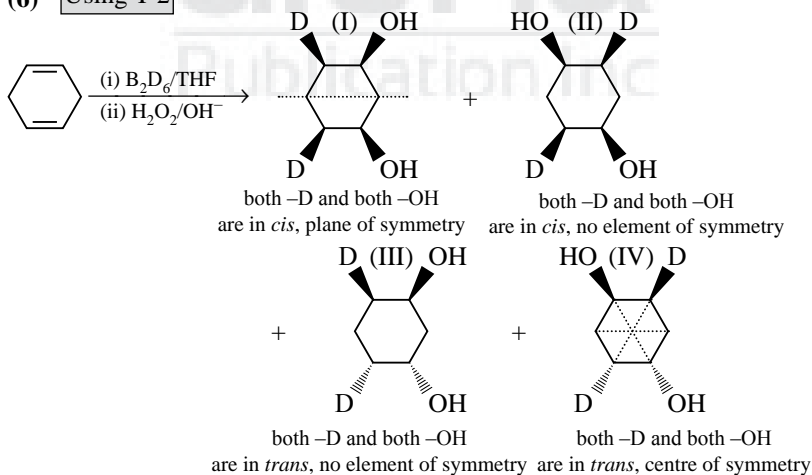


7. (a, b, d) Using T-12

8. (b, c, d) Using T-7



10. (6) Using T-2



Total number of isomeric alcohols = 1 (I) + 2 (II, enantiomers) + 2 (III, enantiomers) + 1 (IV) = 6.