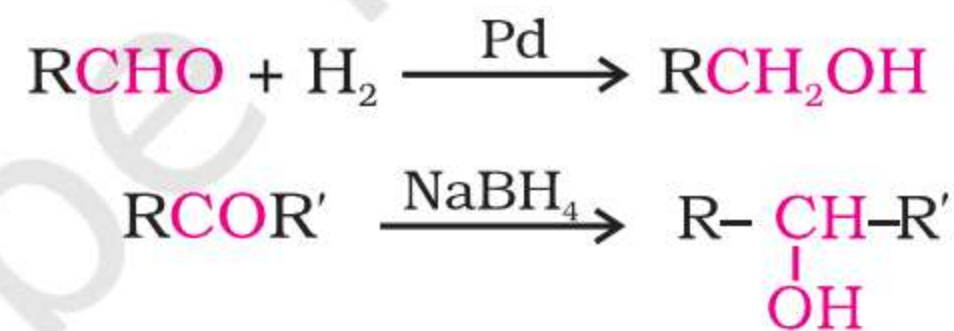


alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

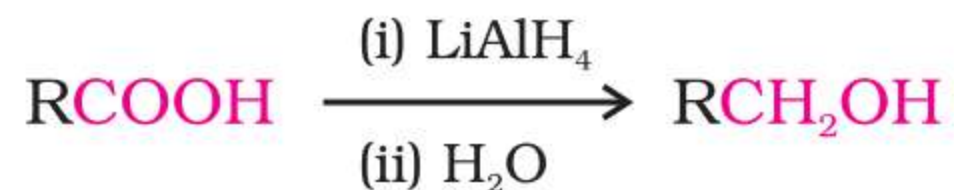
2. From carbonyl compounds

Next
Chapter

- (i) *By reduction of aldehydes and ketones:* Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is a finely divided metal such as platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



- (ii) *By reduction of carboxylic acids and esters:* Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agent.



The numbers in front of the reagents along the arrow indicate that the second reagent is added only when the reaction with first is complete.

However, LiAlH_4 is an expensive reagent, and therefore, used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters (Section



boiling points:

- (a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.
- (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

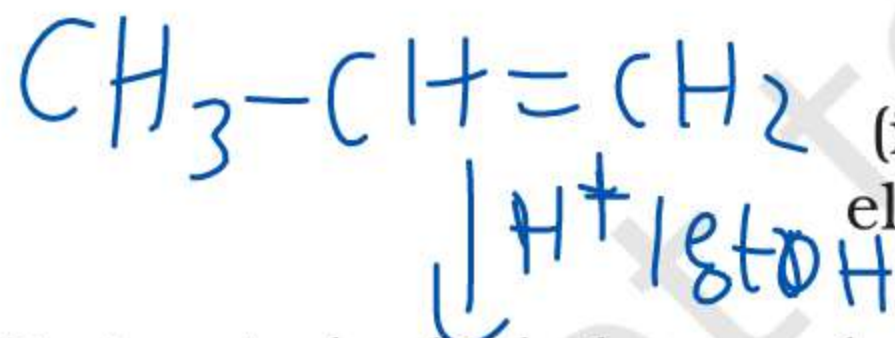
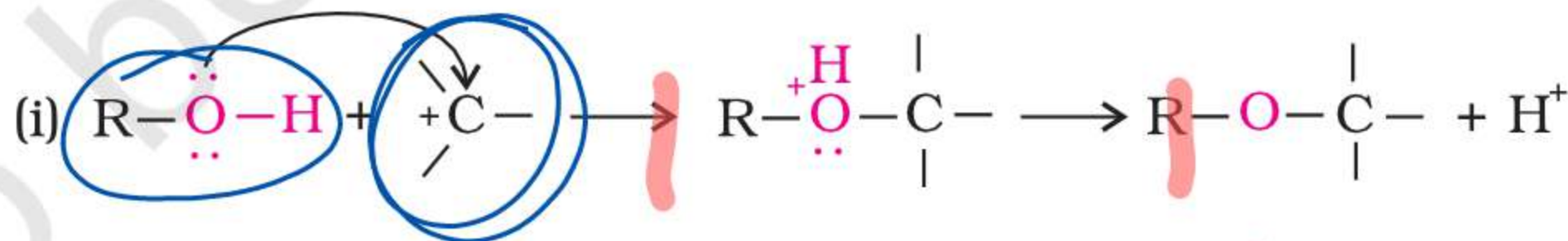
Solution

- (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.
- (b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

11.4.4 Chemical Reactions

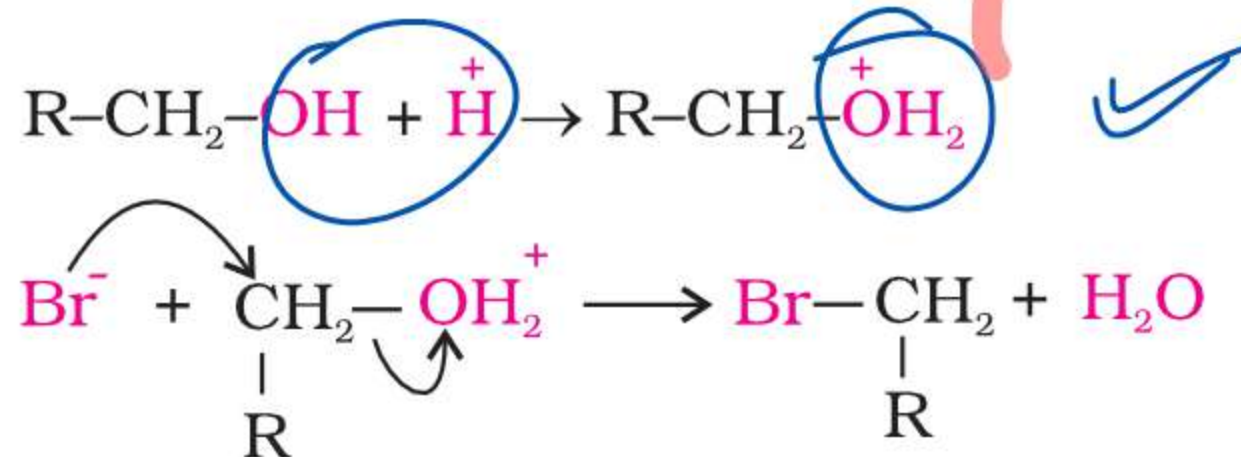
Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O-H is broken when alcohols react as nucleophiles.

Alcohols as nucleophiles



(ii) The bond between C-O is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles



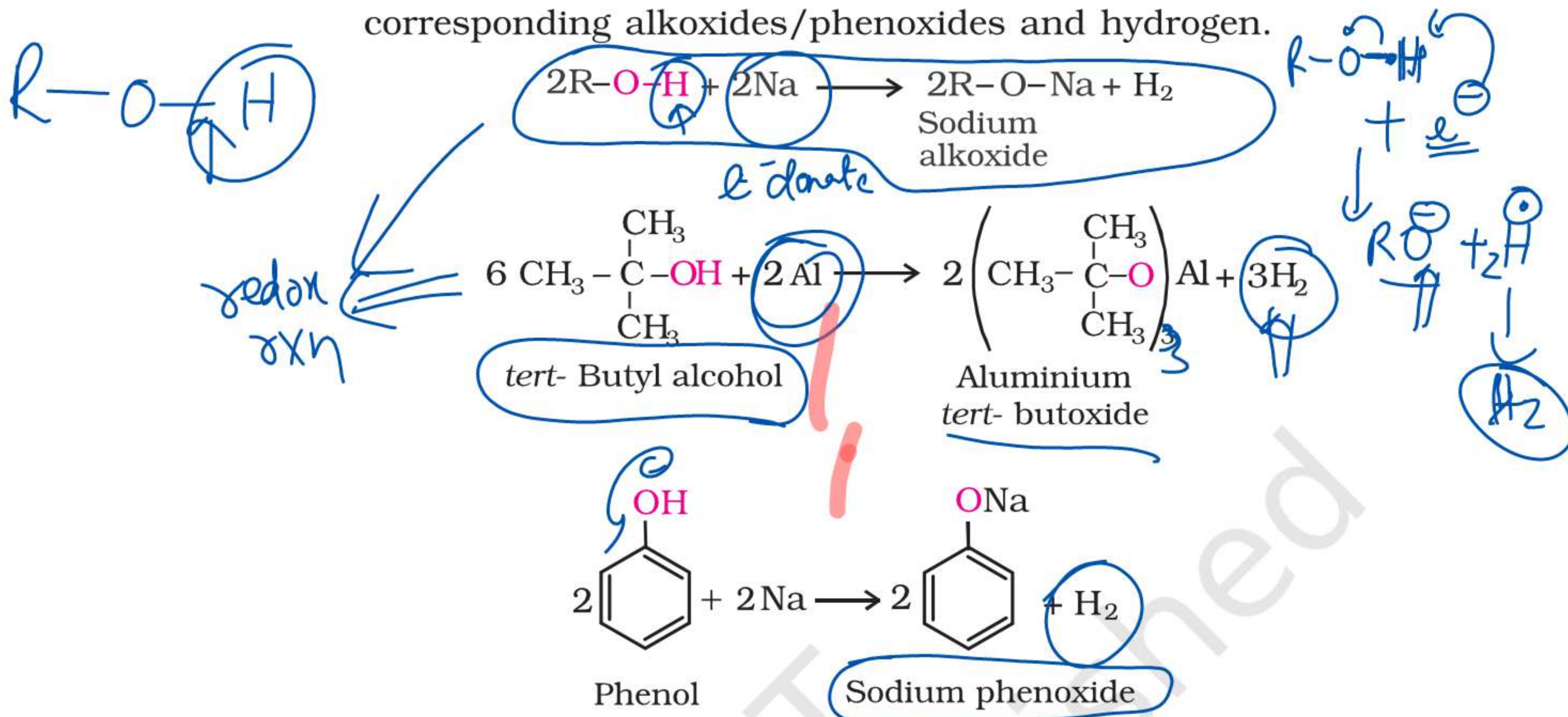
Based on the cleavage of O-H and C-O bonds, the reactions of alcohols and phenols may be divided into two groups:



(a) Reactions involving cleavage of O-H bond

1. Acidity of alcohols and phenols

(i) *Reaction with metals:* Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.



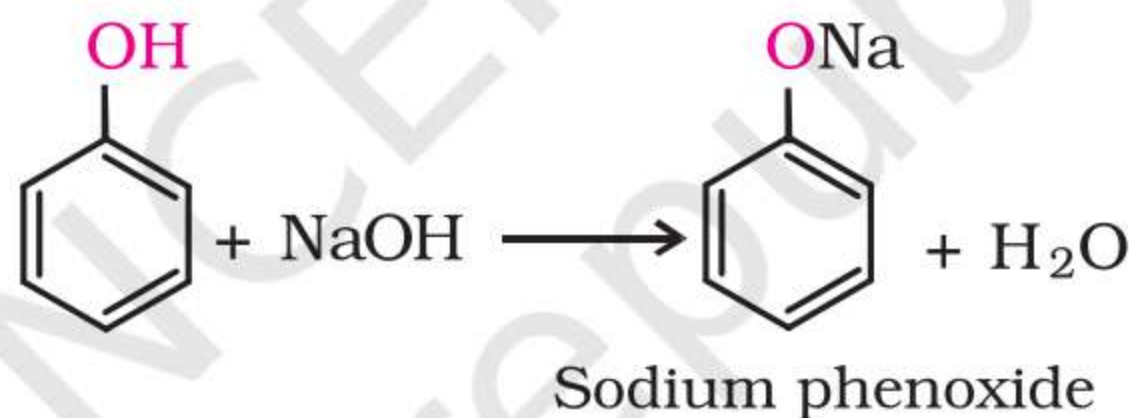
In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



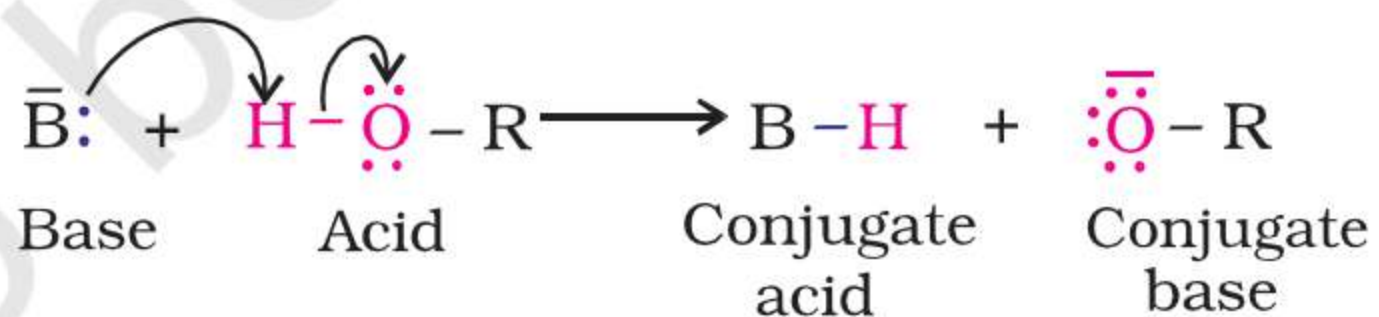
Phenol

Sodium phenoxide

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



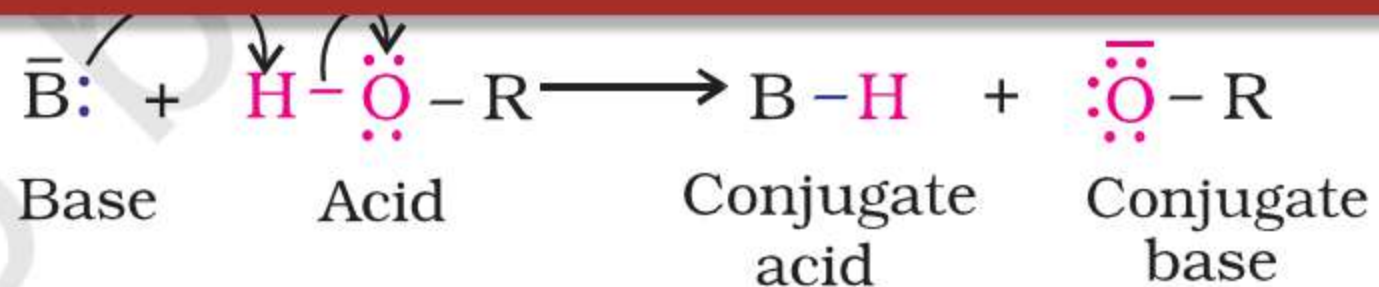
The above reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are Brønsted acids i.e., they can donate a proton to a stronger base (B:).



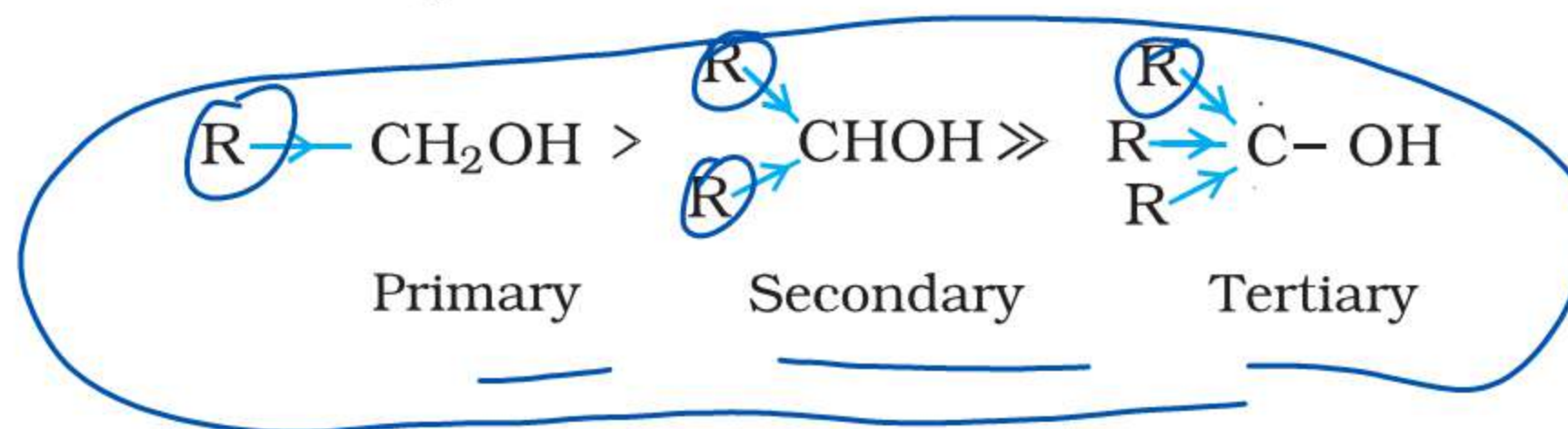
(ii) *Acidity of alcohols:* The acidic character of alcohols is due to the polar nature of O-H bond. An electron-releasing group ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$) increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:

R_1 R_2

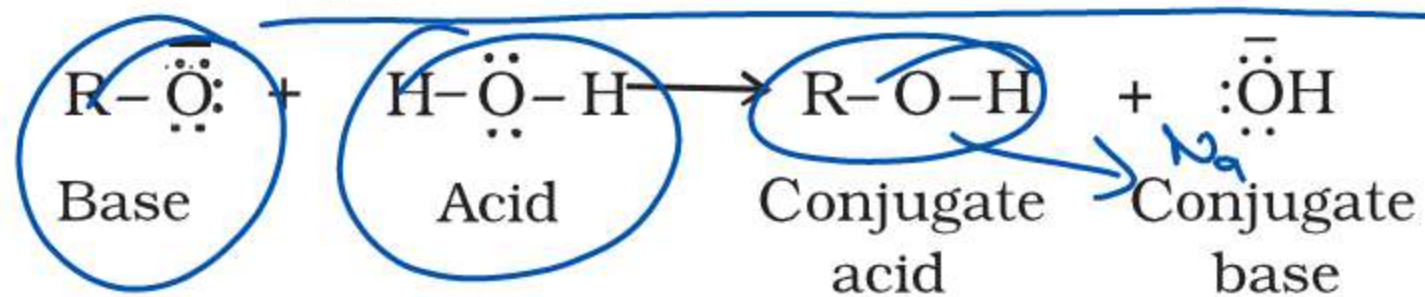




(ii) *Acidity of alcohols:* The acidic character of alcohols is due to the polar nature of O-H bond. An electron-releasing group (-CH₃, -C₂H₅) increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

- (iii) *Acidity of phenols*: The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of -OH group to be positive.



present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

The greater the pK_a value, the weaker the acid.

Table 11.3: pK_a Values of some Phenols and Ethanol

Compound	Formula	pK_a
<i>o</i> -Nitrophenol	$o\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.2
<i>m</i> -Nitrophenol	$m\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	8.3
<i>p</i> -Nitrophenol	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.1
Phenol	$\text{C}_6\text{H}_5\text{-OH}$	10.0
<i>o</i> -Cresol	$o\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
<i>m</i> -Cresol	$m\text{-CH}_3\text{C}_6\text{H}_4\text{-OH}$	10.1
<i>p</i> -Cresol	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.



Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, [Solution](#)
2,4, 6-trinitrophenol.

2. Esterification

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

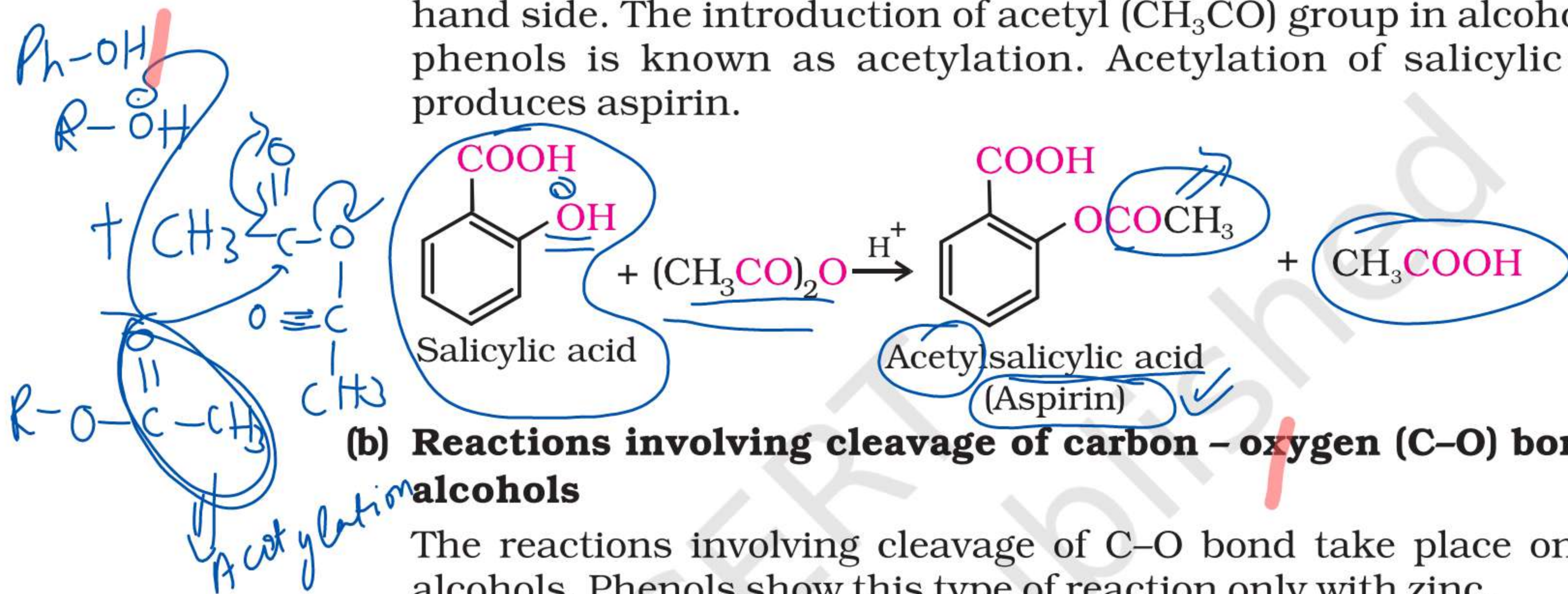
329 Alcohols, Phenols and Ethers

2015-16



analgesic, anti-inflammatory and antipyretic properties.

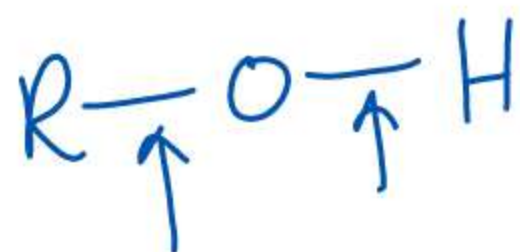
out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



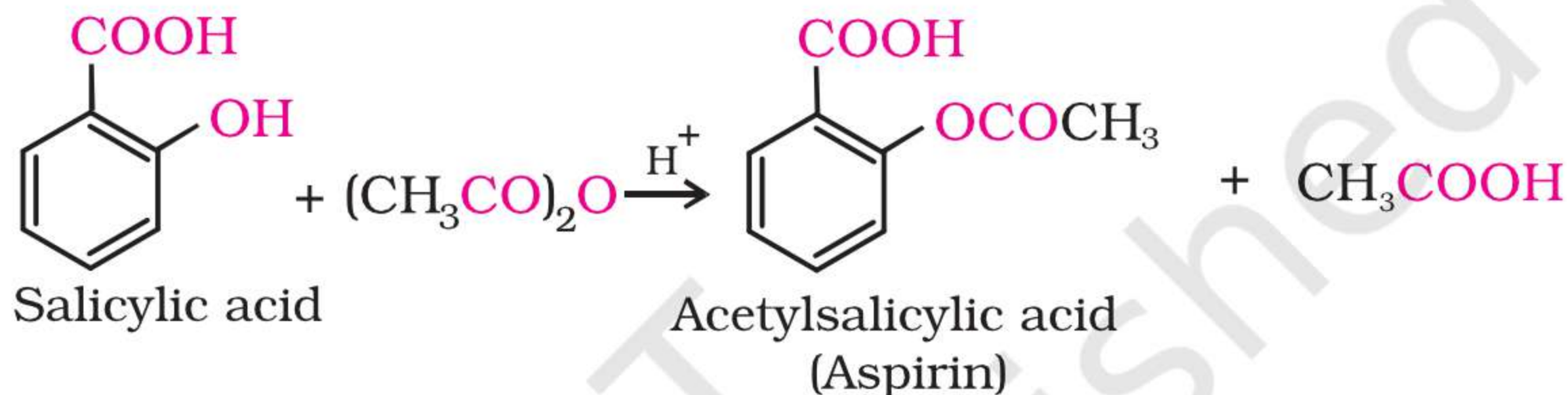
The reactions involving cleavage of C-O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

- 1. Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 10, Class XII).

analgesic, anti-inflammatory and antipyretic properties.



out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



(b) Reactions involving cleavage of carbon - oxygen (C-O) bond in alcohols

The reactions involving cleavage of C-O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

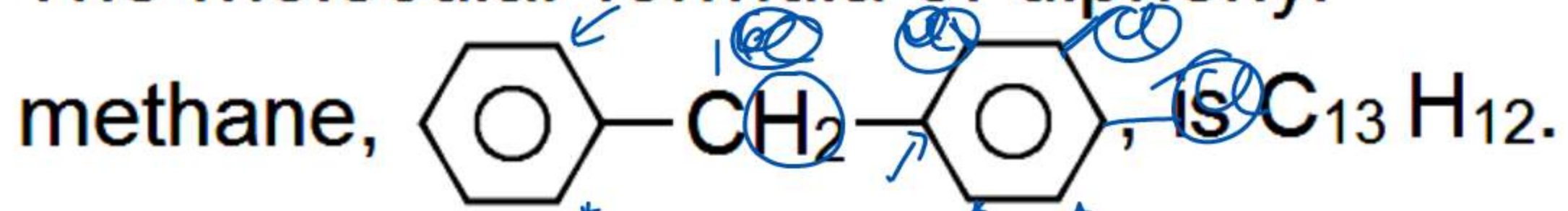
- 1. Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 10, Class XII).



Reactivity order of halides for dehydrohalogenation is

- (1) $R - F > R - Cl > R - Br > R - I$
- (2) $R - I > R - Br > R - Cl > R - F$
- (3) $R - I > R - Cl > R - Br > R - F$
- (4) $R - F > R - I > R - Br > R - Cl$

The molecular formula of diphenyl

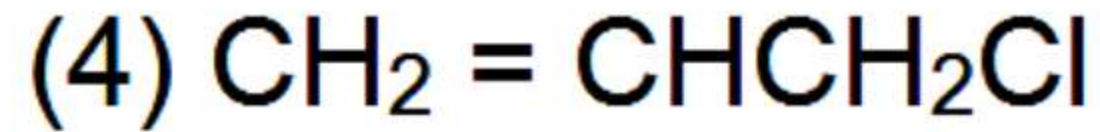
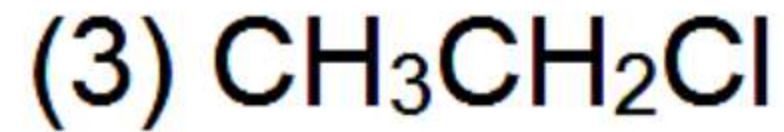
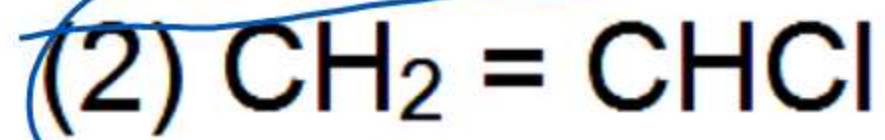
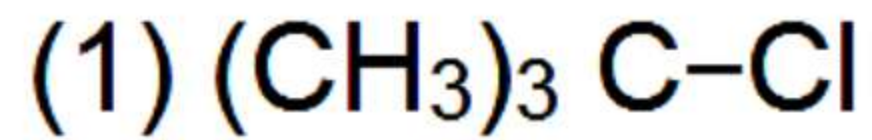


How many structural isomers are possible when one of the hydrogen is replaced by chlorine atom

- ~~(1) 4~~
- (3) 7

- (2) 8
- (4) 6

Which of the following is least reactive in a nucleophilic substitution reaction ?



The major organic product in the reaction,

$\text{CH}_3\text{OCH}(\text{CH}_3)_2 + \text{HI}$ • Product, is/are

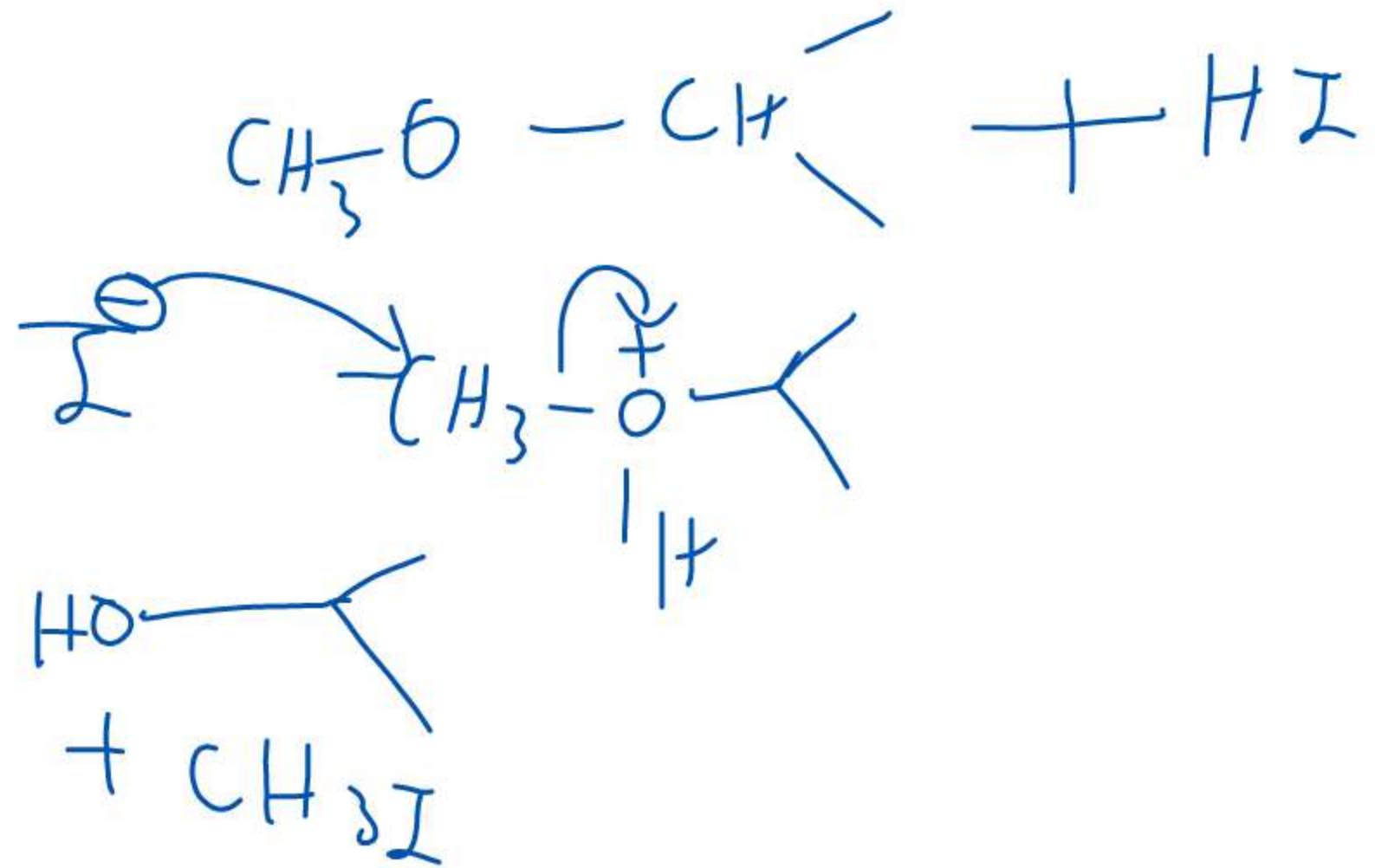
(1) $\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{CHI}$

(2) $\text{ICH}_2\text{OCH}(\text{CH}_3)_2$

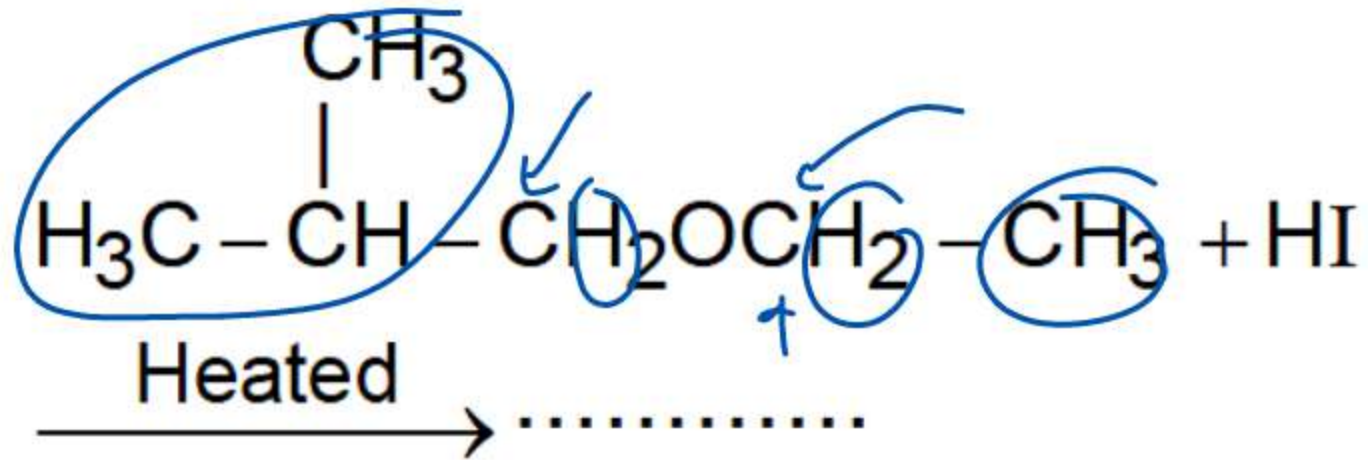
(3) $\text{CH}_3\text{OC}(\text{CH}_3)_2$

I

✓ (4) $\text{CH}_3\text{I} + (\text{CH}_3)_2\text{CHOH}$



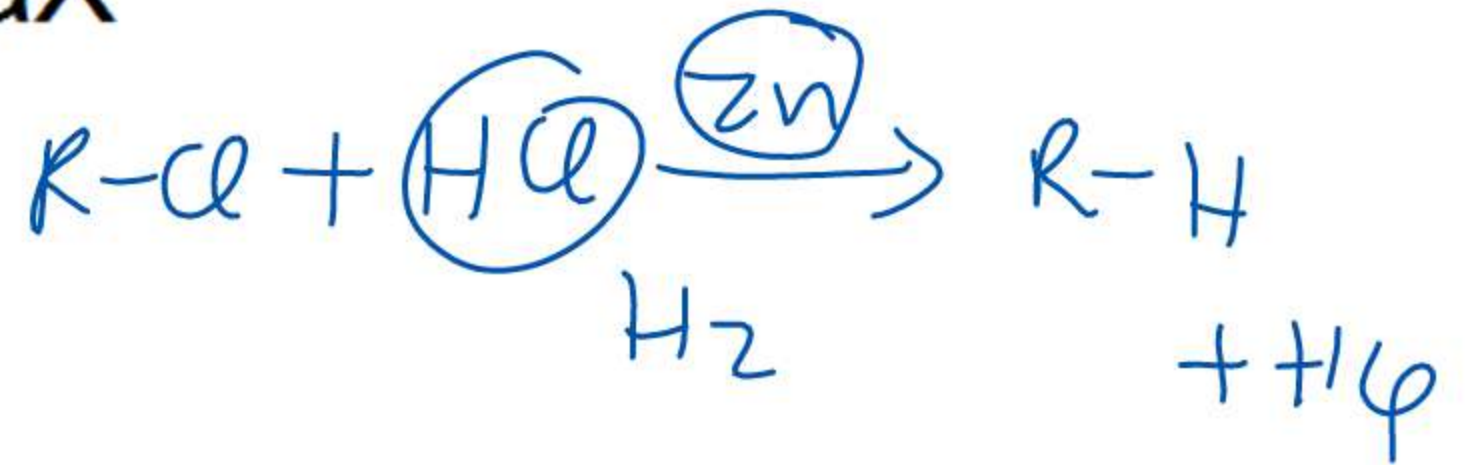
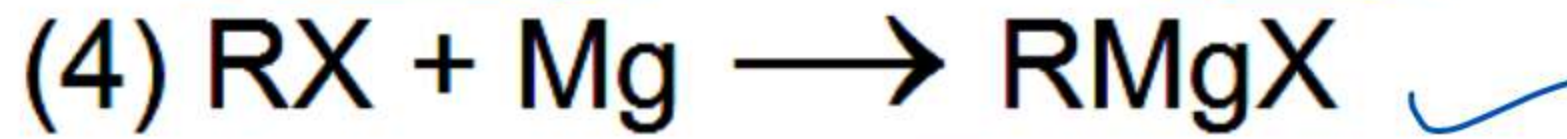
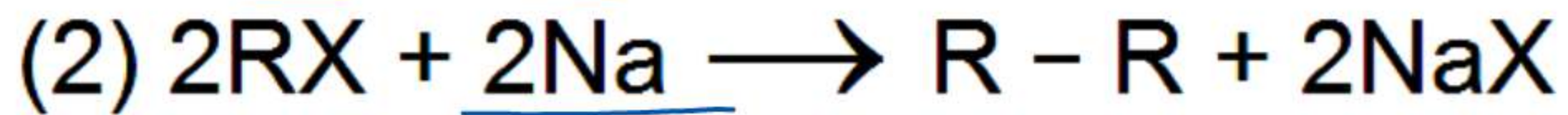
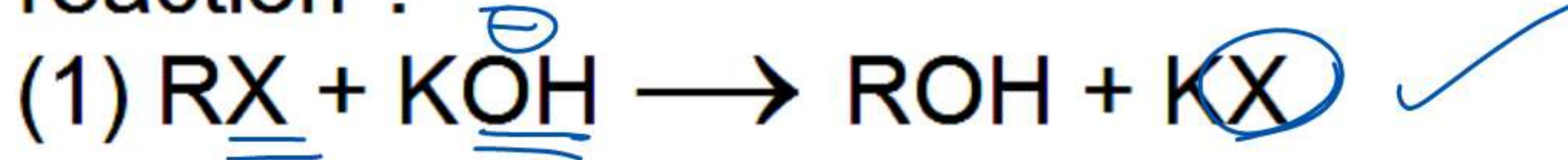
In the reaction which of the following compounds will be formed?



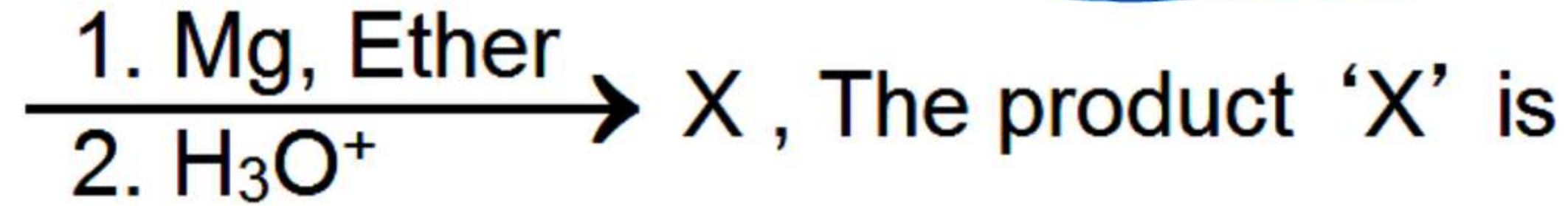
- (1) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{I} + \text{CH}_3\text{CH}_2\text{OH} \end{array}$
- (2) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 + \text{CH}_3\text{CH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array}$
- (3) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- (4) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{I} \end{array}$ ✓



Which of the following reactions is an example of nucleophilic substitution reaction ?




In the following reaction $C_6H_5CH_2Br$

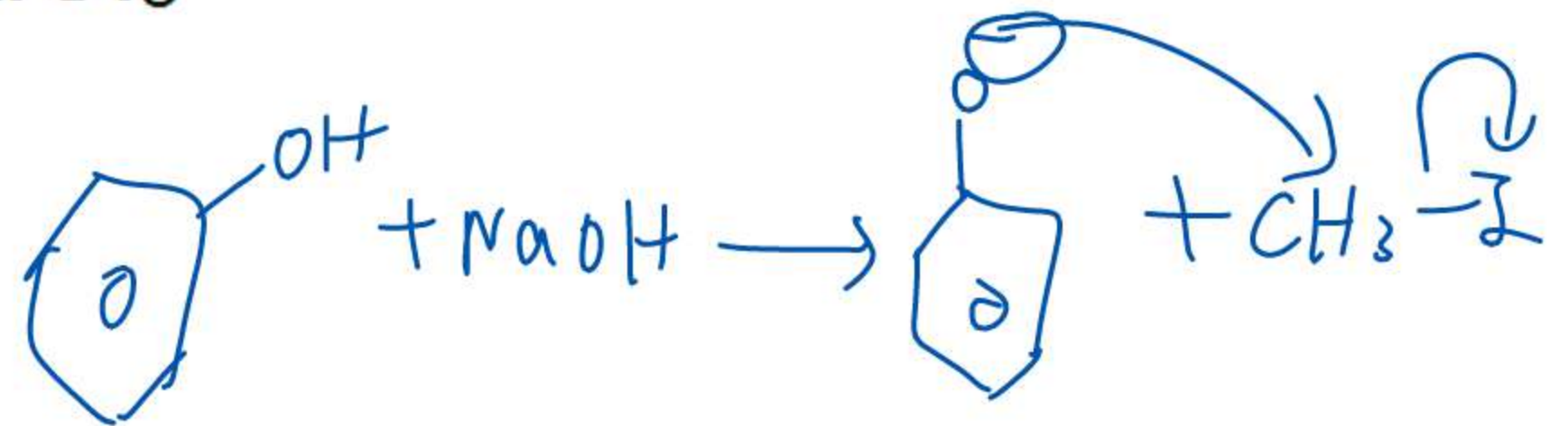
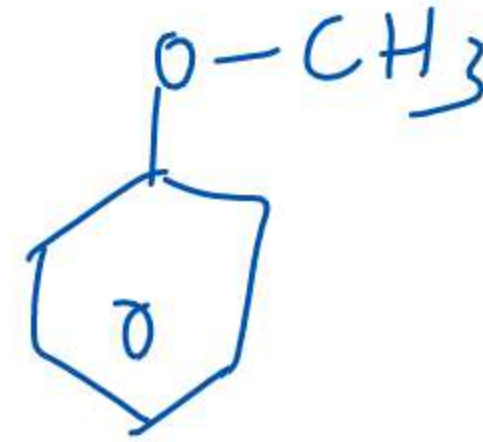


- (1) $C_6H_5CH_2OH$
(2) $C_6H_5CH_3$ ✓
(3) $C_6H_5CH_2CH_2C_6H_5$
(4) $C_6H_5CH_2OCH_2C_6H_5$

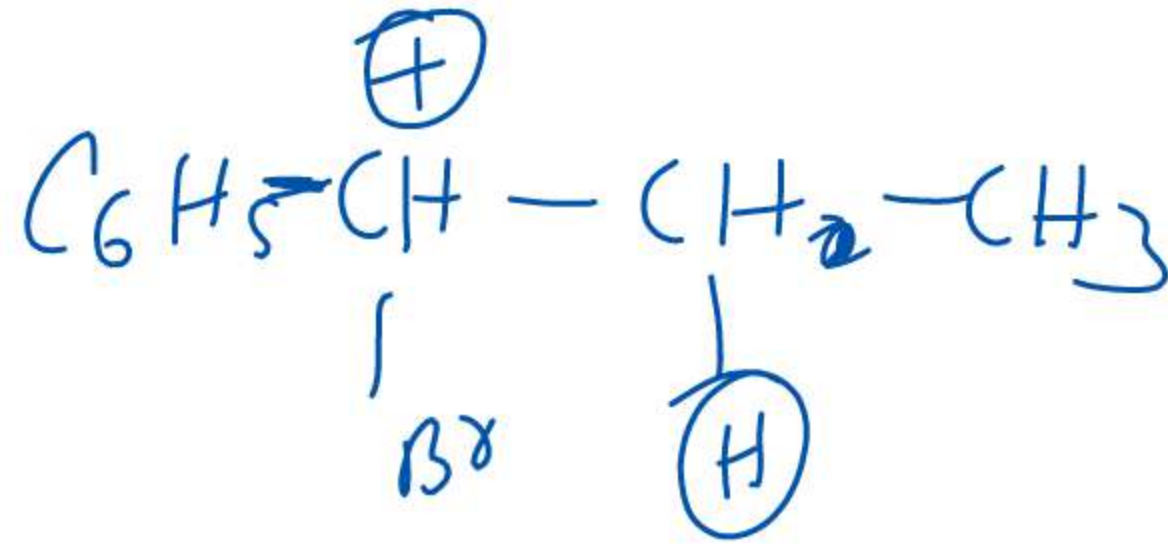
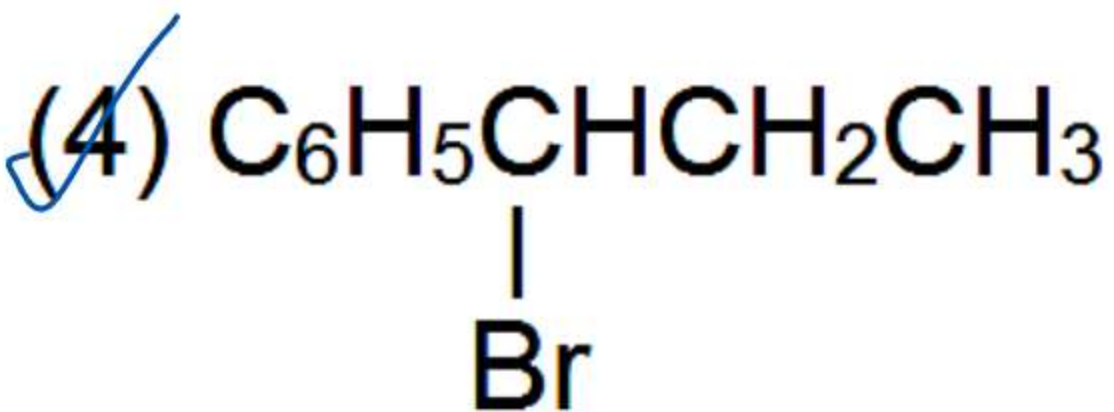
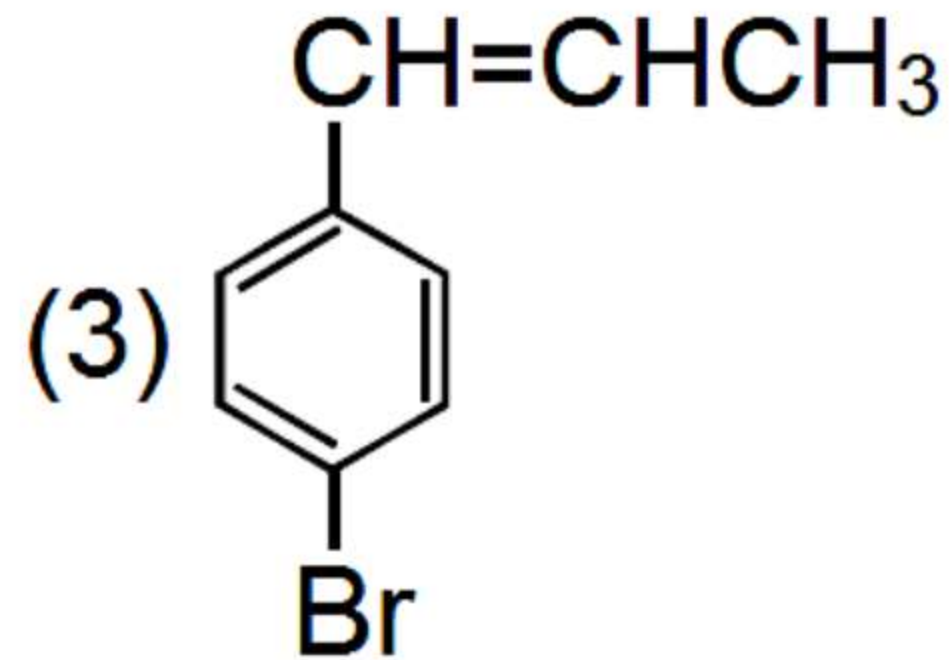
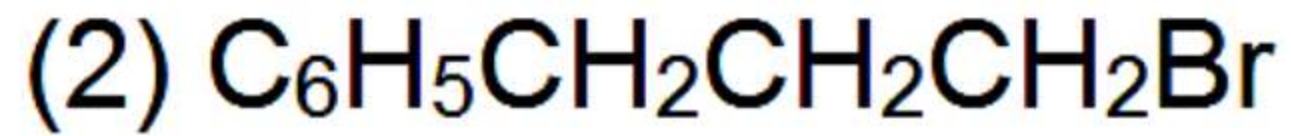
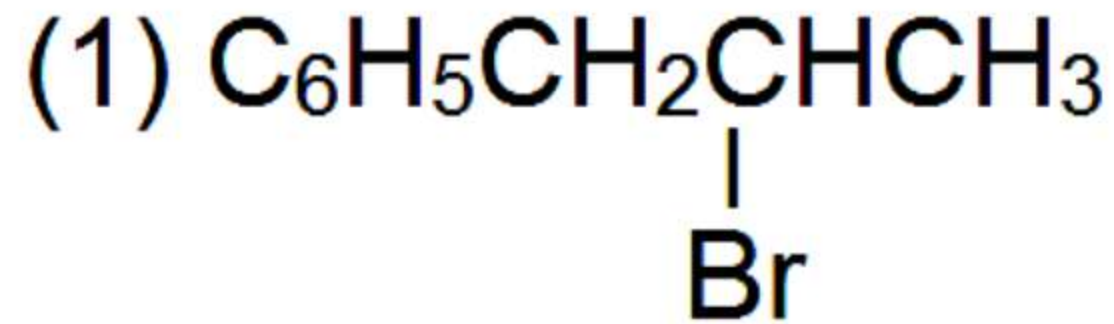


Among the following sets of reaction which one produces anisole?

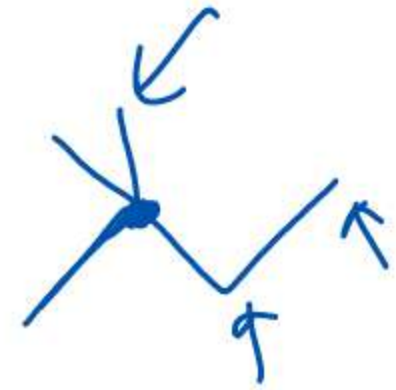
- (1) CH_3CHO ; RMgX
- (2) $\text{C}_6\text{H}_5\text{OH}$; NaOH ; CH_3I 
- (3) $\text{C}_6\text{H}_5\text{OH}$; neutral, FeCl_3
- (4) $\text{C}_6\text{H}_5-\text{CH}_3$; CH_3COCl ; AlCl_3



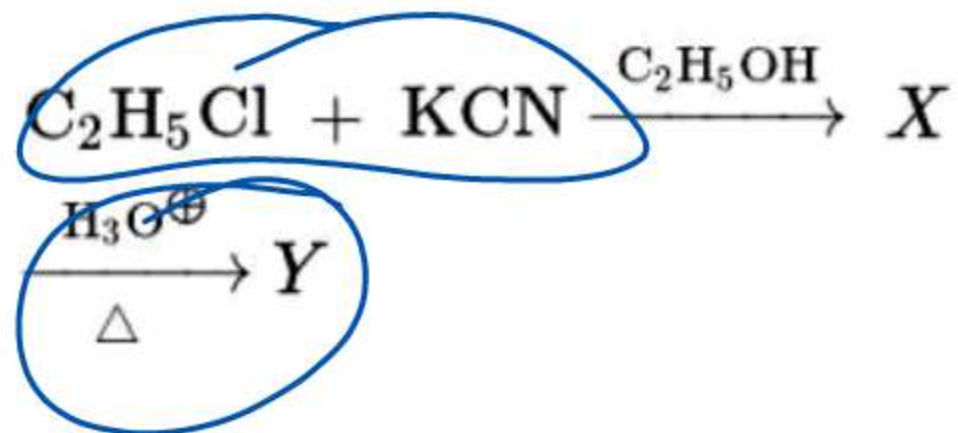
The reaction of $C_6H_5CH=CHCH_3$ with HBr produces :-



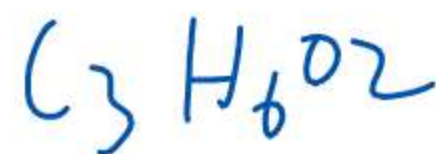
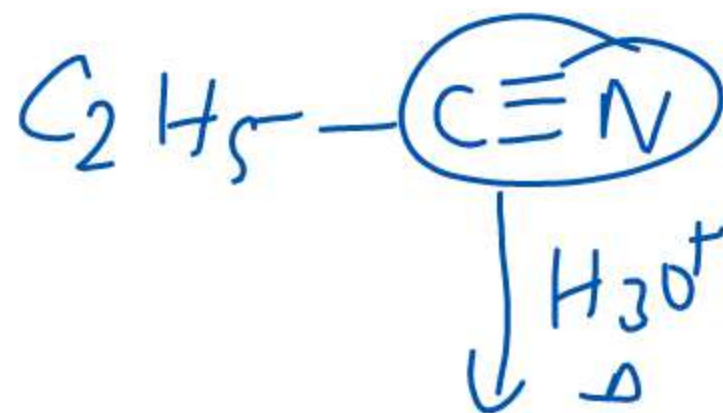
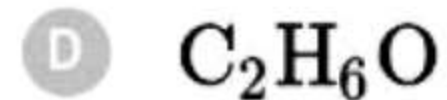
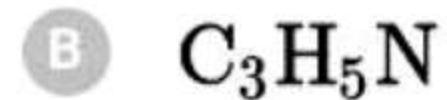
Of the five isomeric hexanes, the isomer which can give only two monochlorinated compounds is (excluding stereoisomers)



In the reaction sequence,



What is the molecular formula of Y?



The S_N2 reaction involves back-side attack and therefore results in a "Walden Inversion." For which one of the substrates shown would you be able to demonstrate that such back-side attack with "Walden Inversion" has in fact occurred?

A 1-bromopropane



B 2-bromobutane

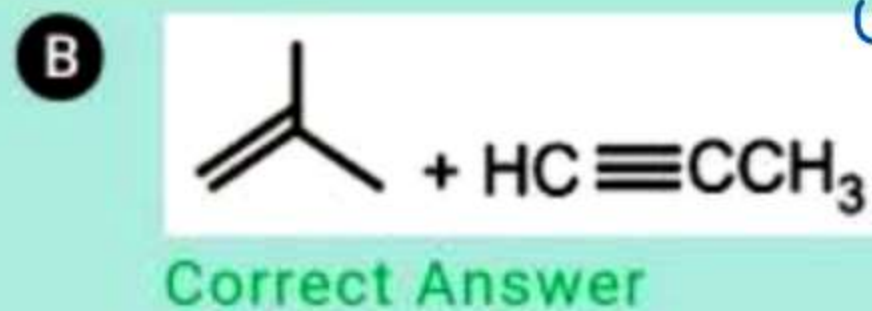
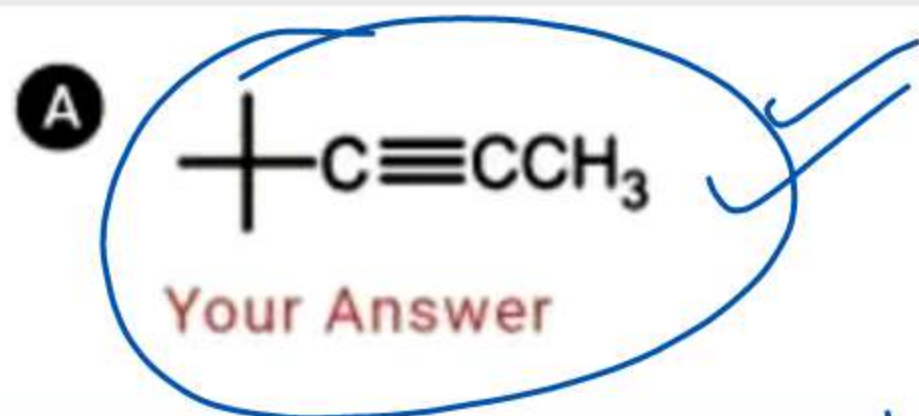
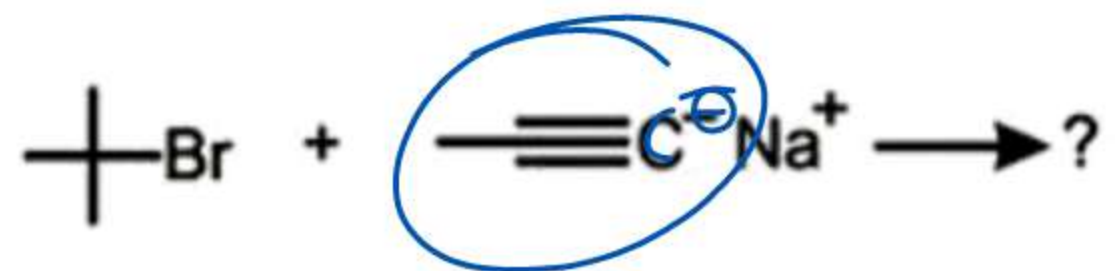


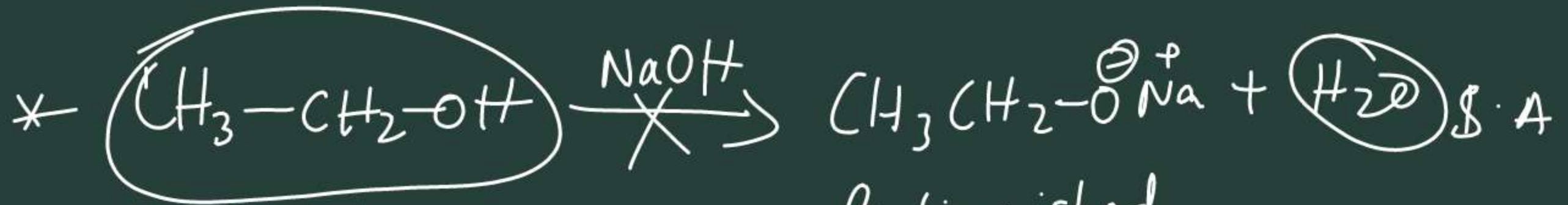
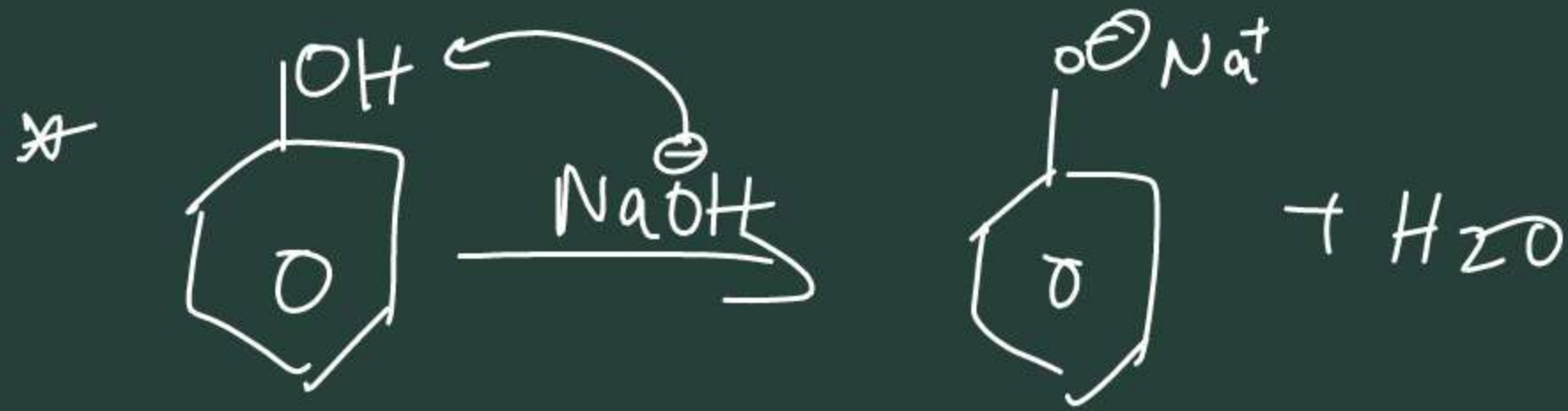
C 3-bromopentane



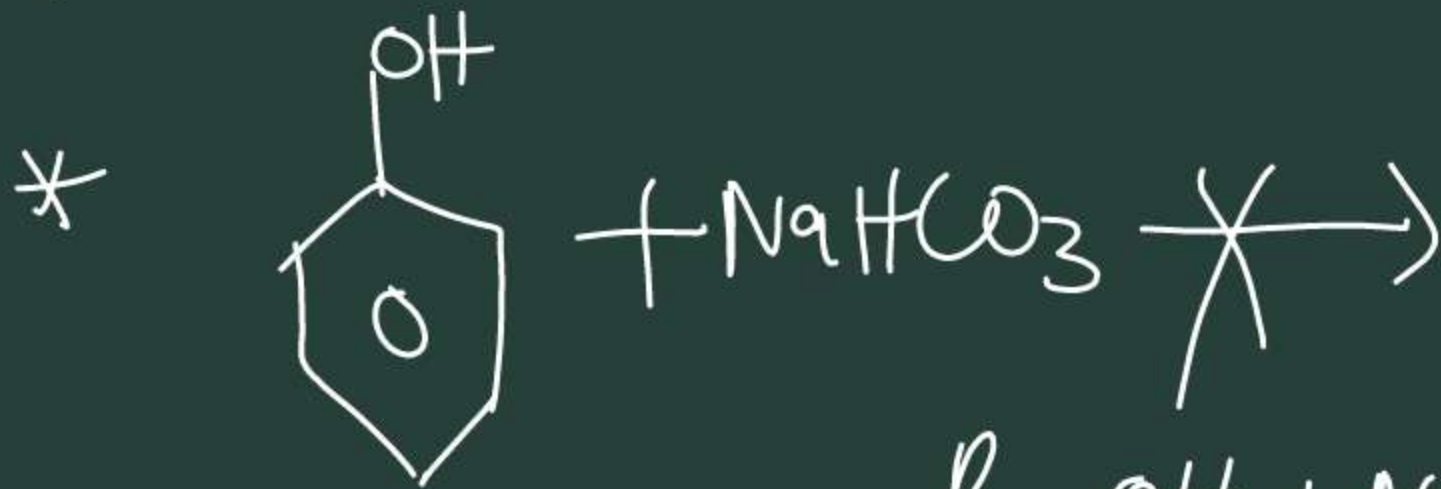
D Methyl bromide

What do you expect to be the main product when tert-butyl bromide reacts in the following manner?

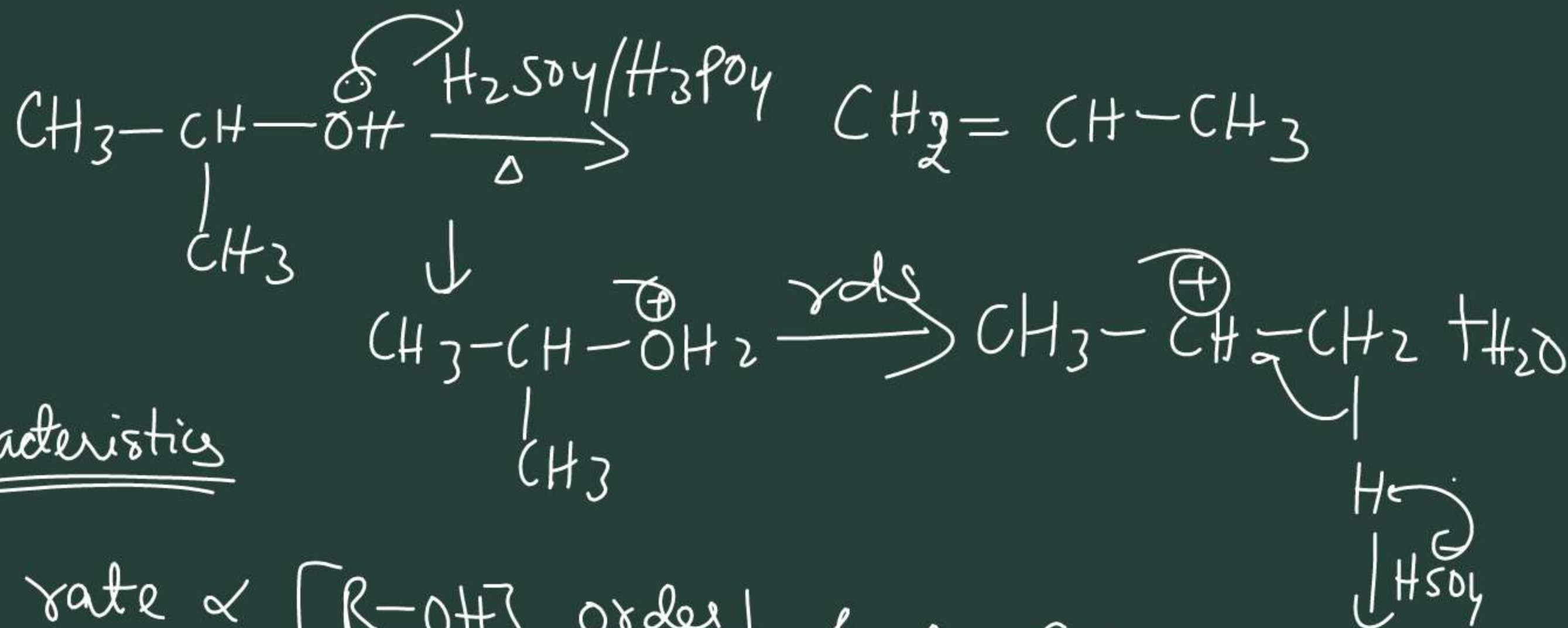




Phenol & Alcohol can be distinguished by using NaOH.



Dehydration of Alcohol (E₁ Mechanism)

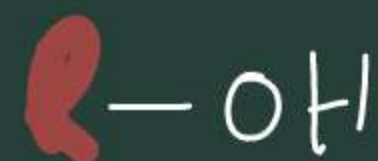


Characteristics

- * rate $\propto [\text{R-OH}]$ order 1 molecularity
- * formation of carbocation is the rds of
- * rearrangement occur.

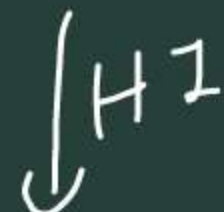
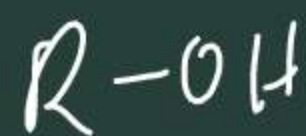
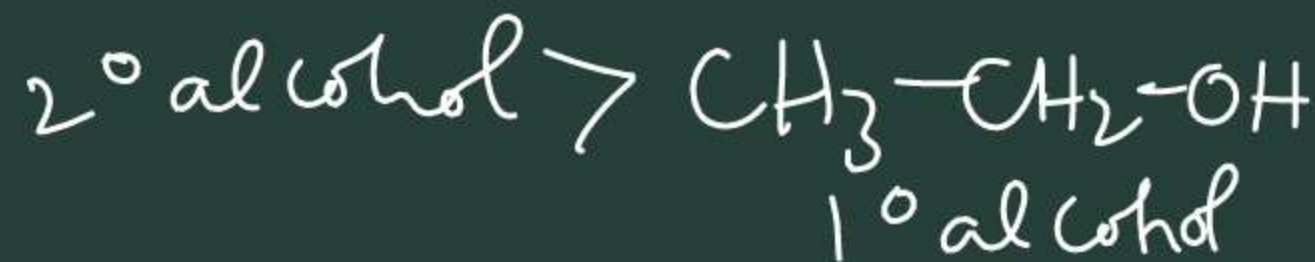
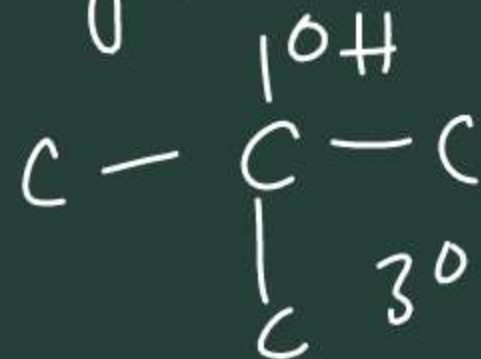
* more stable alkene is major product

* Rate of dehydration



elimination

conc.



Substitution

