

ORGANIC CHEMISTRY

COLLEGE OF EDUCATION FOR PURE SCIENCES

DEPARTMENT OF CHEMISTRY

(SECOND STAGE)

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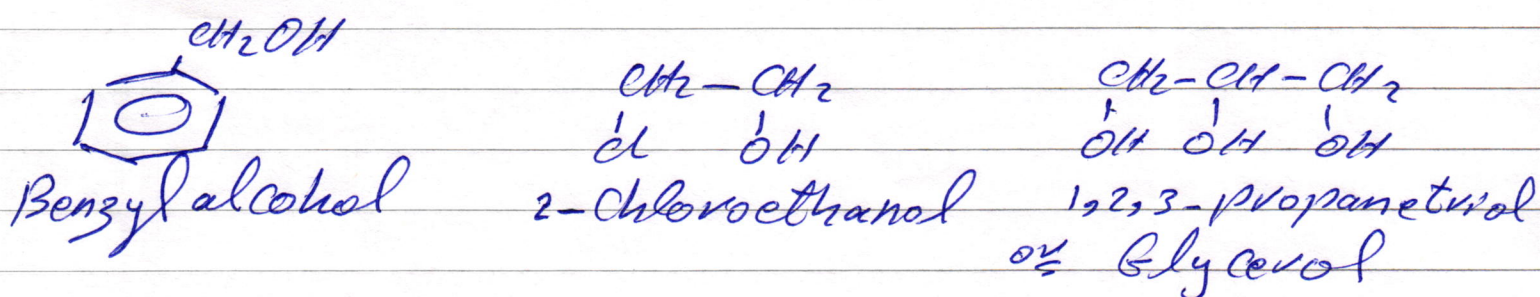
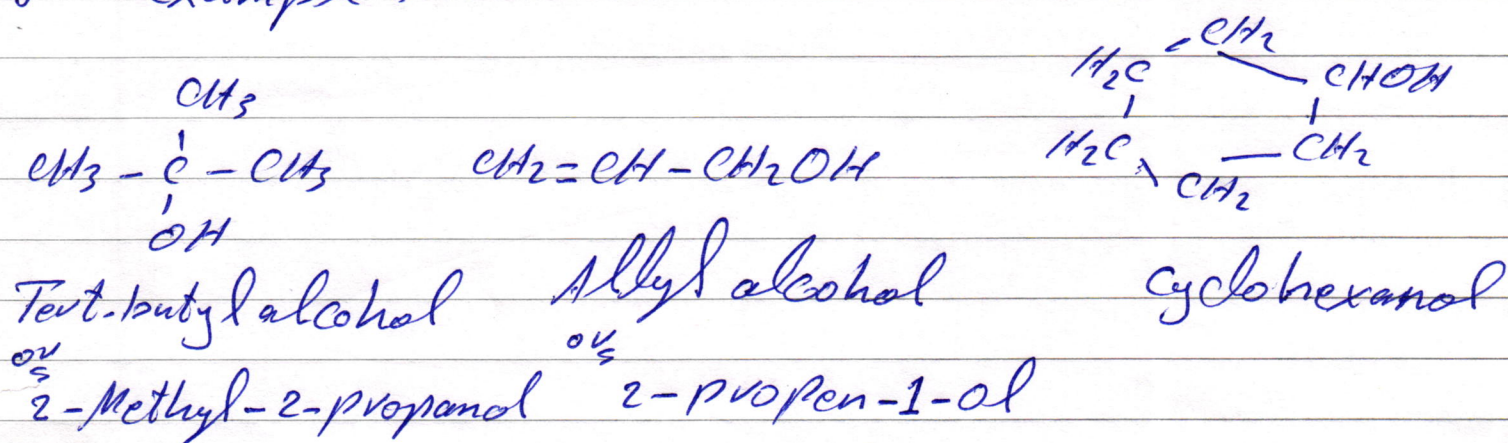
CHAPTER ELEVEN ... ORGANIC SULFUR COMPOUNDS

CHAPTER ONE ...

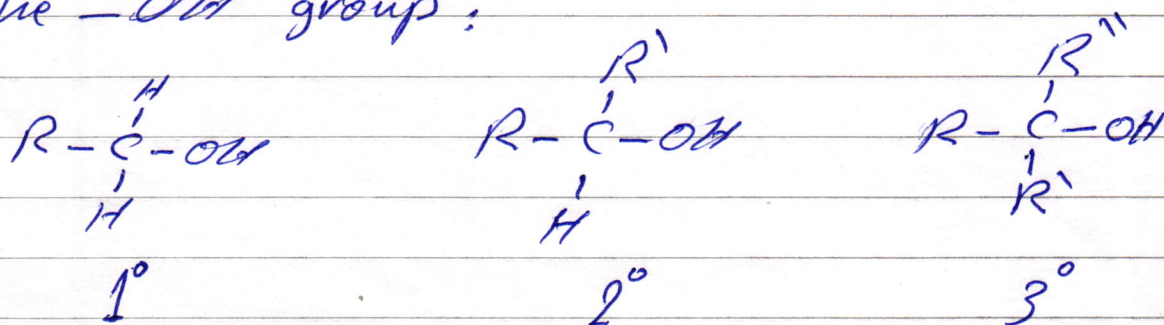
ALCOHOLS

1. Structure of alcohols;

Alcohols are compounds of the general formula ROH , where R is any alkyl or substituted alkyl group. The group may be primary, secondary or tertiary; it may be open chain or cyclic; it may contain a halogen atom, additional hydroxyls, or one of the many groups that are still unfamiliar to us; a double bond, or an aromatic ring, for example;

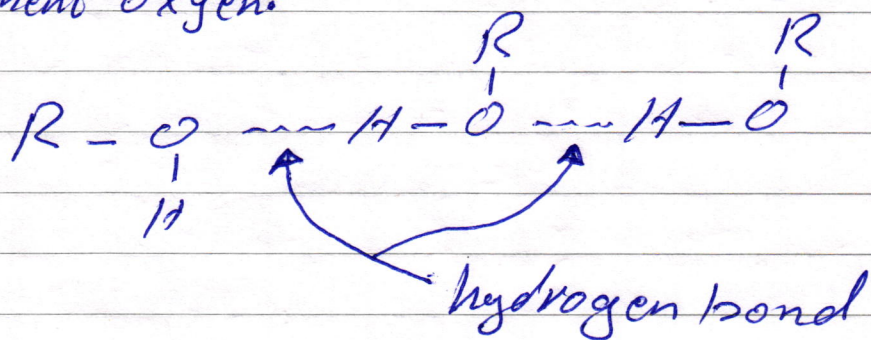


An alcohol is classified as primary, secondary and tertiary, according to the kind of carbon that bears the $-OH$ group:



2. Physical properties of alcohols

The hydroxyl group is quite polar and most important, contains hydrogen bonded to the highly electronegative element oxygen.



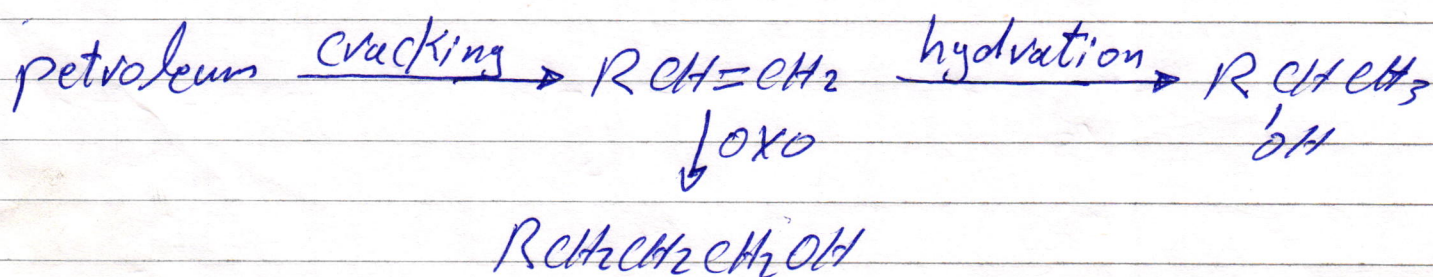
The boiling point of alcohols are almost highest from n-alkane, ethers, alkyl halide, aldehyde and water because present the hydrogen bond.

3. Industrial source of alcohols

There are three principal ways to get the simple alcohols that are the back-bone of aliphatic organic synthesis, ways that can utilize all our sources of organic raw material - petroleum, natural gas, coal and the biomass.

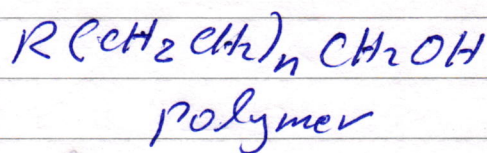
These methods are:

- a - by hydration of alkenes
- b - by the oxo process from alkenes
- c - by fermentation of carbohydrates



petroleum cracking $\rightarrow R-CH=CH_2$

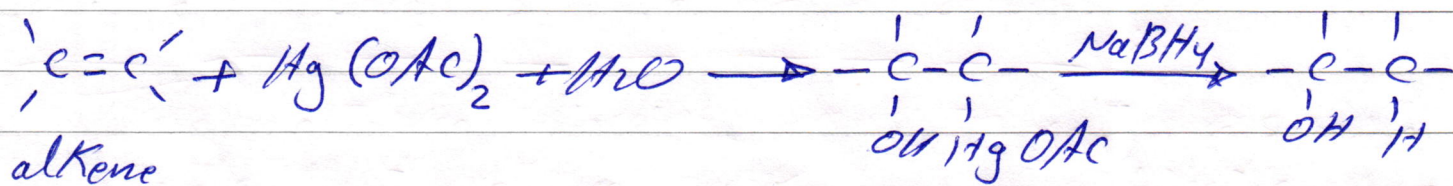
\downarrow polymerization



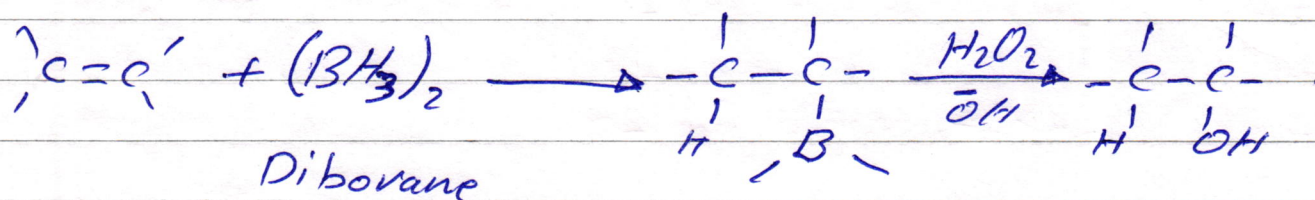
Sugars $\xrightarrow{\text{Yeast fermentation}}$ CH_3CH_2OH
ethyl alcohol

4. Preparation of alcohols :

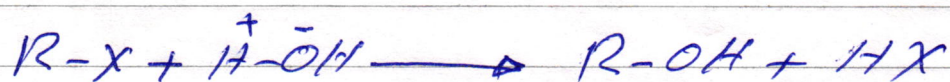
1- Oxymercuration - demercuration :



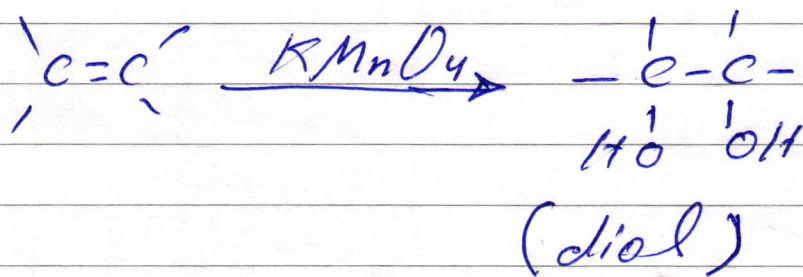
2- Hydroboration - oxidation :



3- Hydrolysis of alkyl halide :

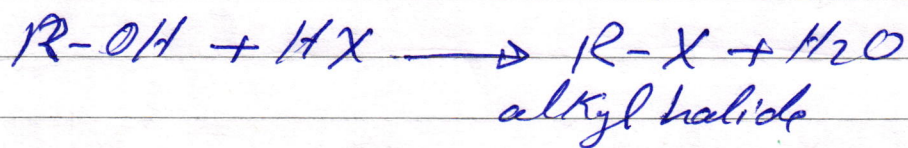


4- Oxidation of alkenes:

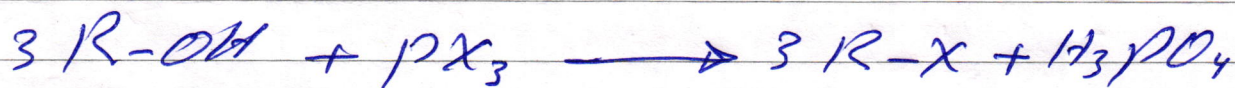


5. Reactions of alcohols:

1- Reaction with hydrogen halide:

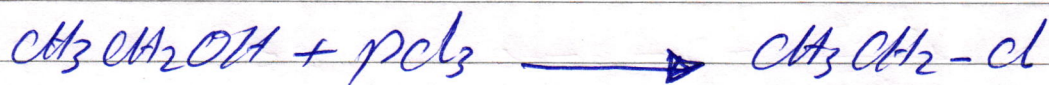


2- Reaction with phosphorus trihalides:

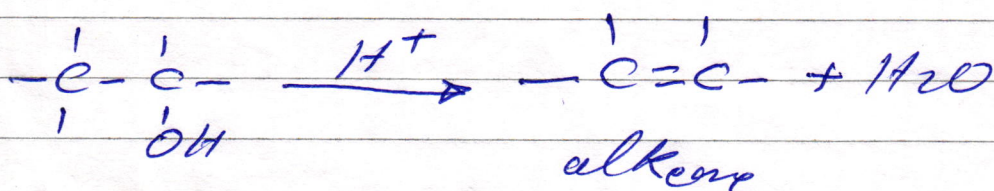


where: PX_3 : PBr_3 or PCl_3 , PI_3

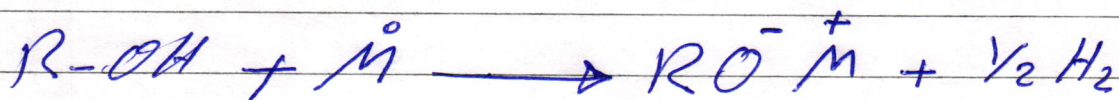
ex:



3- Dehydration:

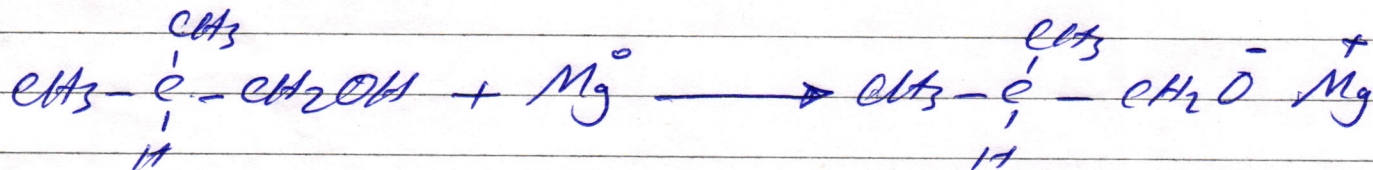
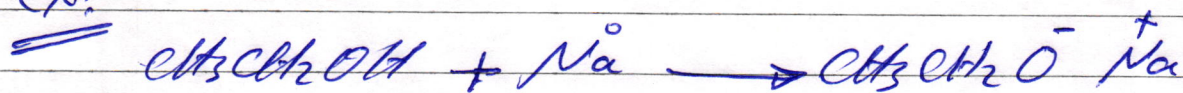


4 - Reaction with active metals :

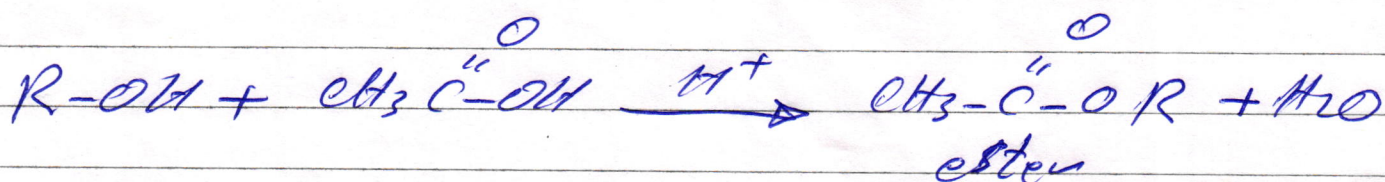
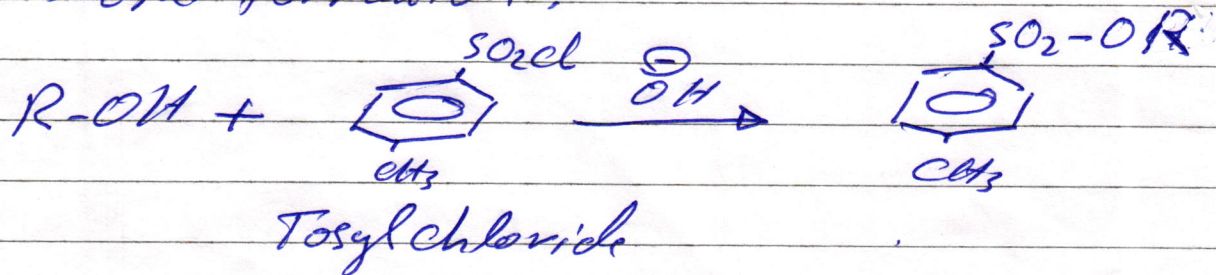


where M is Na, K, Mg, Al, ... etc.

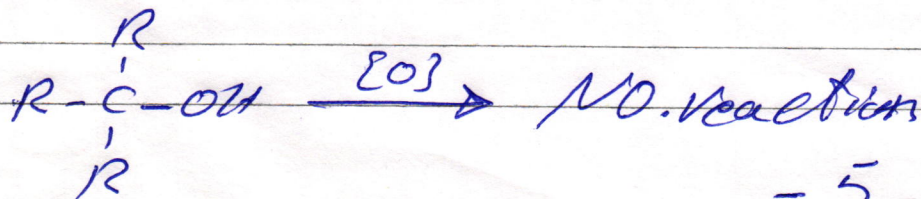
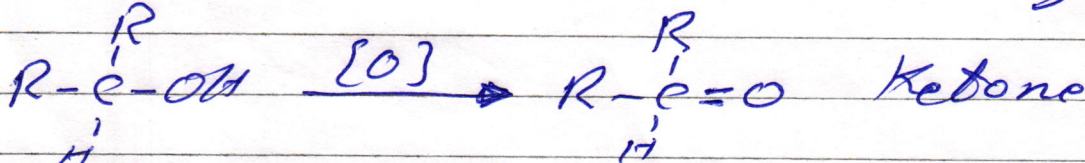
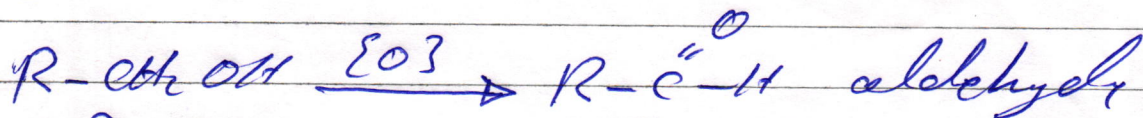
ex:



5 - Ester formation :



6 - Oxidation :



Problems:

Q / Show all steps in a possible laboratory synthesis of each of the following from n-butyl alcohol:

1. n-butyl bromide
2. sodium n-butoxide
3. n-butyraldehyde

Q / Starting from alcohols of four carbons atom or fewer and making use of any necessary solvent or reagents to synthesis for each compounds:

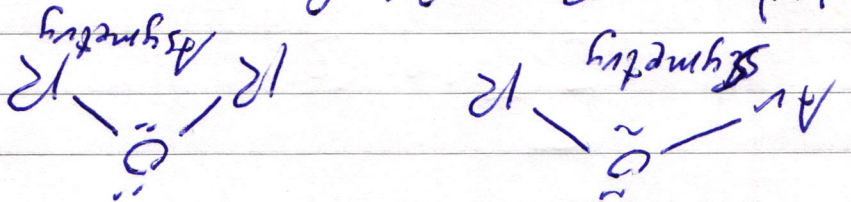
1. 2-chloropropane
2. ethyl tosylate
3. potassium tert.-butoxide

CHAPTER TWO ...

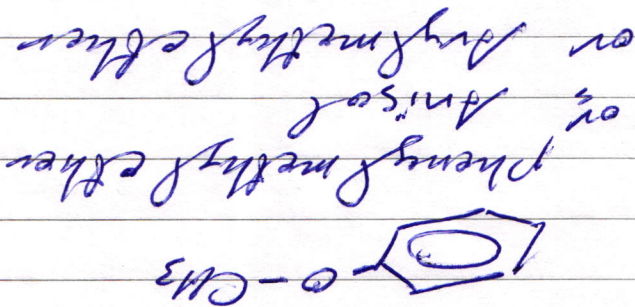
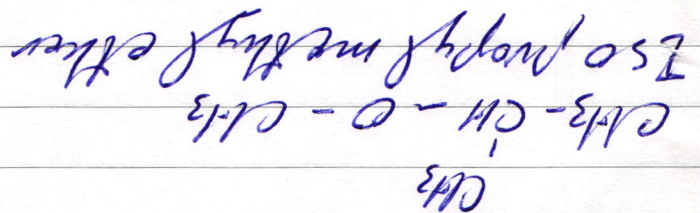
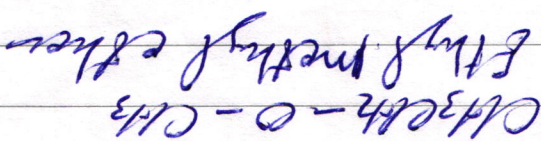
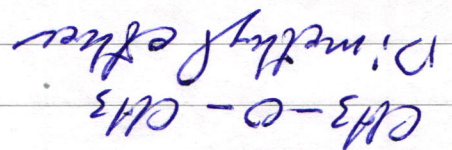
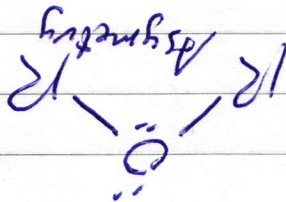
ETHERS

A1 Structures & Nomenclature:

Ethers, Can be derived from alcohols after replace the hydrogen atom, by alkyl group.



Where: R = alkyl group or any group.



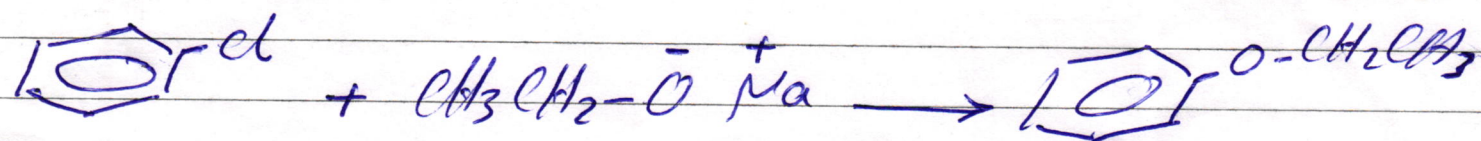
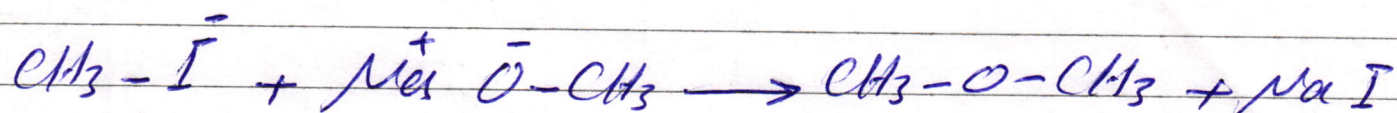
B / Physical properties:

Ether molecular don't contain on hydrogen atom joint with oxygen atom that contain high electro-negative charge, so that, ethers will be boiling in a low degree from alcohols, because not contain on hydrogen bonding.

Preparation of Ethers

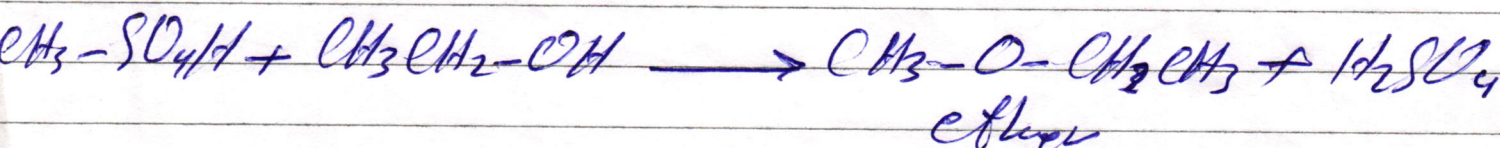
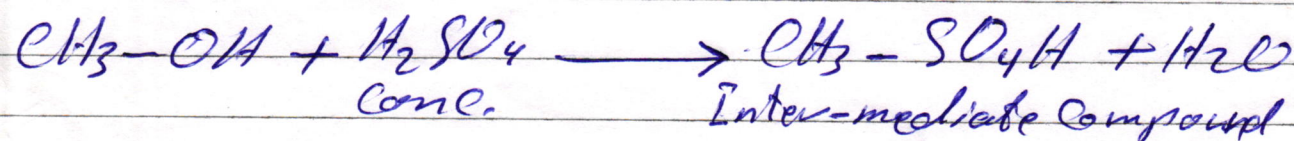
① From alkyl halide:

alkyl halide will be reacted with sodium alkoxide to produce symmetry or asymmetry ethers.



② From alcohols:

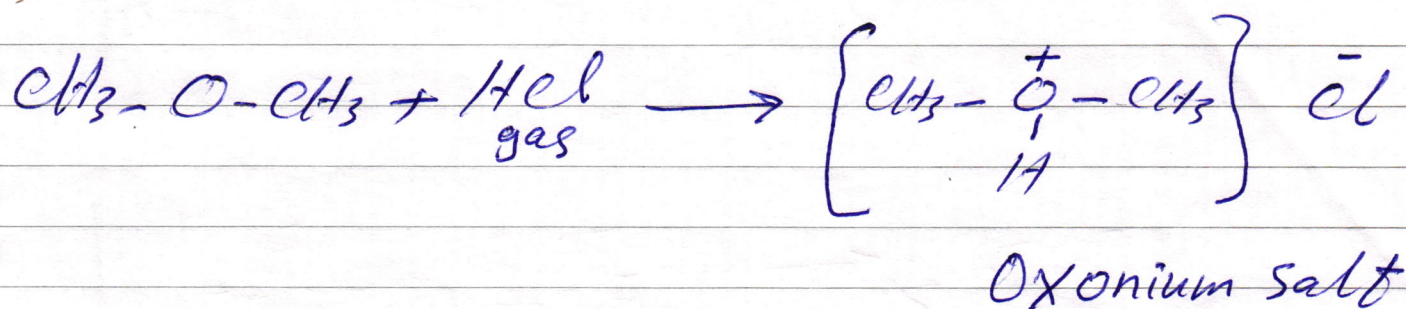
This reaction contains two steps; the first, is reacted alcohol with concentrated sulphuric acid to produce the inter-mediate compound; the second step, the inter-mediate compound will be react with another molecules from alcohol to produce ether.



D/ Reactions of Ethers

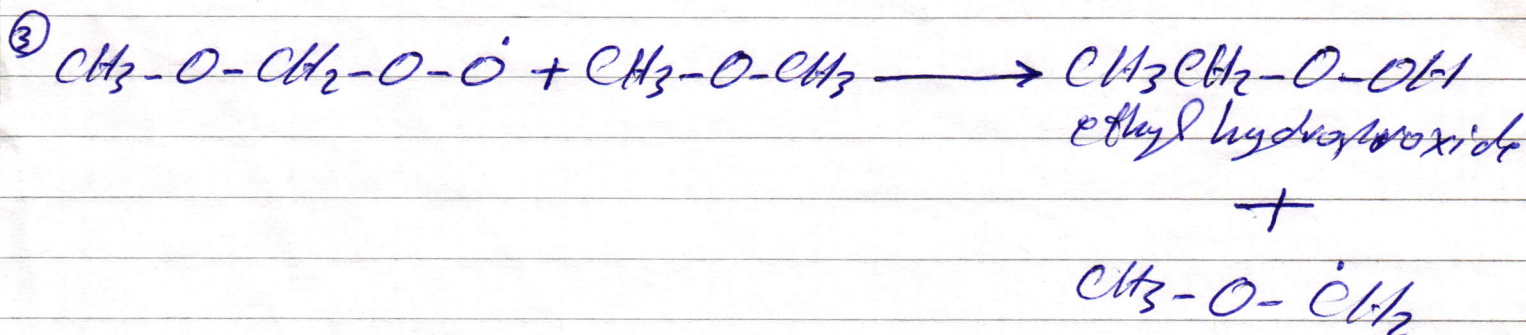
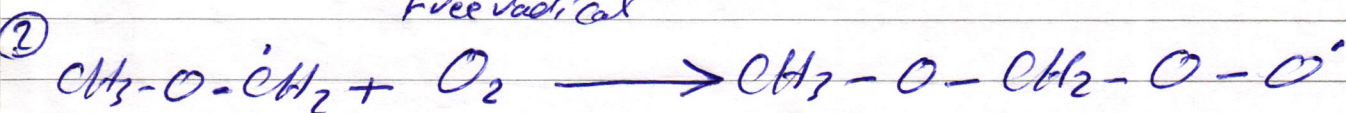
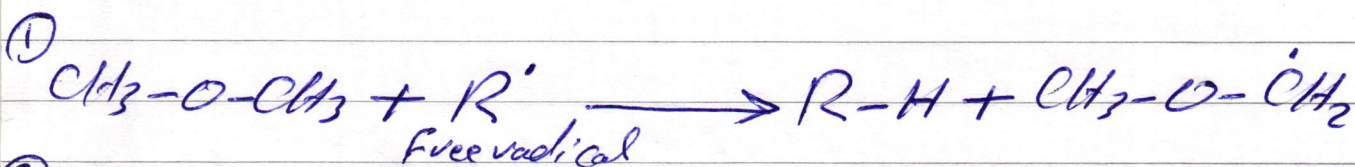
* Ethers are low reactivity, because contain an oxygen atom joint with two alkyl groups.

① React with mineral acids:



② Oxidation:

Ethers will be reacted with oxygen air to produce hydroperoxide and self-oxidation occurs by method of free radical mechanism.



CHAPTER THREE ...

ARYL HALIDES