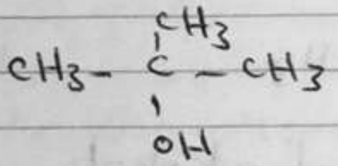
Wafaa alkoofee

Alcohols:- $C_nH_{2n+2}O$

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

R–OH An Alcohol (functional group –OH)

of many groups that are still unfamiliar to us: a double bond, for example.



$CH_2=CH-CH_2OH$

Allyl alcohol

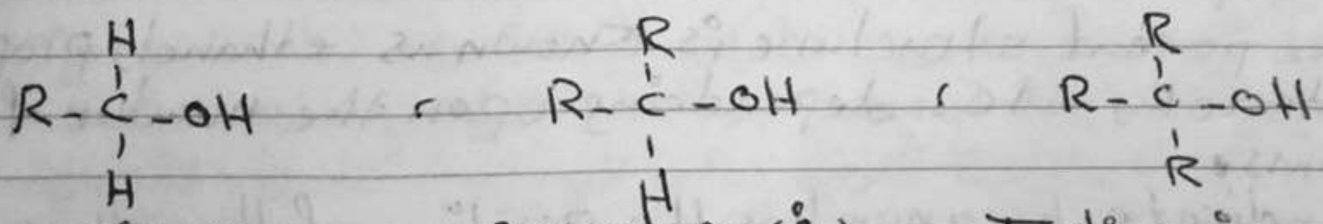
2-propen-1-ol

Common tert-butyl alcohol

IUPAC 2-Methyl-2-propanol

classification of alcohols:-

An alcohol is classified as primary, secondary or tertiary according to the kind of carbon that bears the –OH group.



1° primary, secondary (2°), Tertiary 3°

Nomenclature of alcohols

Alcohols are named by two principal system. For the simpler alcohols the common names are most often used. A common name consists simply of the name of the alkyl group followed by the word alcohol. For example:-

CH_3CH_2OH
Ethyl alcohol
(1°) primary alcohol

CH_3CHCH_3 (with OH on the middle C)
(2°)
Isopropyl alcohol

$CH_3-CH(CH_3)-CH_2OH$
Isobutyl alcohol

$CH_3-C(CH_3)(OH)-CH_3$
tert. Butyl alcohol

The most versatile system is, of course, the IUPAC the rules are:-

1- Select as the parent structure the longest continuous carbon chain that contains the $-OH$ group; then consider the compound to have been derived from this structure by replacement of hydrogen by various group.
The parent structure is known as ethanol, propanol butanol, etc. depending upon the number of carbo atoms.

2- Indicate by a number the position of the $-OH$ group in the parent chain, generally using the lowest possible number for this purpose.

3- Indicate by numbers the positions of other groups attached to the parent chain.

for example :-

CH_3OH
Methanol

$CH_3CH_2CH_2OH$
1-propanol

$CH_3-CH(OH)-CH_2Br$
1-Bromo-2-propanol

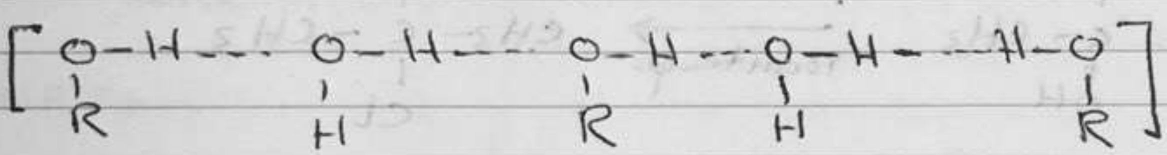
$CH_2(OH)-CH_2(OH)$
1,2-Ethanediol

$CH_3-CH(OH)-CH(CH_3)-CH_3$
3-Methyl-2-butanol

$CH_3-C(CH_3)_2-CH_2OH$
2,2-diMethyl-1-propanol

- physical properties of alcohols :-

- الكحولات سوائل عديمة اللون ، ذات طعم حرق ، وكثافة أقل من كثافة الماء ، وتزداد درجة غليانها B.p مع زيادة الوزن الجزيئي
- تكون درجة غليان الكحولات عالية عند مقارنتها مع الهيدروكاربونات التي لها نفس الوزن الجزيئي وذلك بسبب تكتلها بالاواصر الهيدروجينية



(أواصر هيدروجينية)

- تتناقص قابلية ذوبان الكحولات في الماء مع ازدياد وزنها الجزيئي (اي بزيادة عدد ذرات الكاربون في مجموعة الالكيل (R) الى الحد الذي تصبح فيه عديمة الذوبان .
- كلما كبر حجم مجموعة الألكيل في الكحول يزداد تنافرها مع الماء ويقل امتزاجها ثم ينعدم ذوبانها . حيث ان الافراد الاولى من الكحولات تذوب في الماء نتيجة تكوين اواصر هيدروجينية فكحول المثيل والاثيل جيدة الذوبان بالماء ، بينما كحول البروبيل والبيوتيل معتدلة في الذوبان في حين كحول البنتيل والهكسيل لا تذوب بالماء .

- تسلك الكحولات سلوكاً مشابهاً للماء من حيث الحامضية والقاعدية فهي تسلك سلوك كل من الحوامض الضعيفة والقواعد الضعيفة .

الكحولات كقواعد :- تكتسب الكحولات البروتون بواسطة الاحماض القوية وتكون ايونات

$$R-\ddot{O}-H \rightleftharpoons R-\overset{H}{\underset{..}{O}}{}^{\oplus}-H \quad X^{\ominus}$$

. ROH_2^+ Oxonium

Reactions of Alcohols :-

1- Reactions with hydrogen halides.

$$R-OH + HX \longrightarrow R-X + H_2O$$

Reactivity of HX: HI > HBr > HCl

Reactivity of R-OH :- benzyl > 3° > 2° > 1°

Ex:

$$CH_3-CH(OH)-CH_3 \xrightarrow[\text{or } H_2SO_4 \text{ or } NaBr]{\text{conc. HBr}} CH_3-CH(Br)-CH_3$$

Isopropyl alcohol → Isopropyl bromide

$$CH_3-C(CH_3)(OH)-CH_3 \xrightarrow[\text{room temp.}]{\text{Conc. HCl}} CH_3-C(CH_3)(Cl)-CH_3$$

tert-Butyl alcohol → tert-Buty chloride

2- Reaction with phosphorus trihalides

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

$(PX_3 = PBr_3, PI_3)$

Ex:

$$CH_3-CH_2-CH(CH_3)CH_2OH \xrightarrow{PBr_3} CH_3-CH_2-CH(CH_3)CH_2Br$$

2-Methyl-1-butanol → 2-Methy-1-bromobutane

3- Dehydration

Reactivity ROH: 3° > 2° > 1°

$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \xrightarrow{\text{acid}} -C=C- + H_2O$$

O--H Bond cleavage

RofH انشطار

4- Reaction as acids: reaction with active metals.

$$R\text{-}OH + M \longrightarrow R\overset{-}{O}\overset{+}{M} + \tfrac{1}{2}H_2$$

M = Na, K, Mg, Al, etc...

Reactivity of ROH: $CH_3OH > 1^\circ > 2^\circ > 3^\circ$

Ex:-

$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^{\ominus}Na^{\oplus} + \tfrac{1}{2}H_2$$

Ethyl alcohol → sod- ethoxide

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OH \xrightarrow{K} CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}O^{\ominus}K^{+} + \tfrac{1}{2}H_2$$

tert- Butyl Alcohol

5- Ester formation

Example:-

$$CH_3CH_2OH + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \xrightarrow{H^+} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5 + H_2O$$

Acetic acid

6- Oxidation

- primary (1°) $R\text{-}CH_2OH$
  - $\xrightarrow{CrO_3Cl^+}$ $R\overset{O}{\overset{\|}{C}}\text{-}H$ An aldehyde
  - $\xrightarrow{KMnO_4}$ $R\text{-}COOH$ A carboxylic Acid

- Secondary (2°) $$R\text{-}\overset{R}{C}HOH \xrightarrow[\text{or } CrO_3]{K_2Cr_2O_7} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$$ Ketone

- Tertiary (3°) $$R\text{-}\underset{R}{\overset{R}{C}}\text{-}OH \xrightarrow{KMnO_4} \text{No reaction}$$

Ethers $R-O-R$

Structure and nomenclature of ethers

Ethers are compounds of the general formula ($R-O-R$) (R: Aliphatic group).

To name ethers we usually name the two groups that are attached to oxygen, and follow these names by the word ether:-

$C_2H_5-O-C_2H_5$ — Diethyether

$CH_3-\overset{CH_3}{\overset{|}{C}H}-O-\overset{CH_3}{\overset{|}{C}H}-CH_3$ — Diisopropyl ether

$CH_3-O-C_2H_5$ — Ethyl Methyether

If one group has no simple name, the compound may be named as an (alkoxy) derivative:-

Alkyl + oxygen → Alkoxy ⟹ Methoxy

CH_3-O- (Methyl + oxygen) → Methoxy

$\overset{6}{C}H_3-\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H(OCH_3)\overset{2}{C}H_2\overset{1}{C}H_3$

3-Methoxy hexane

$CH_2(OH)-CH_2(OC_2H_5)$

2-Ethoxyethanol

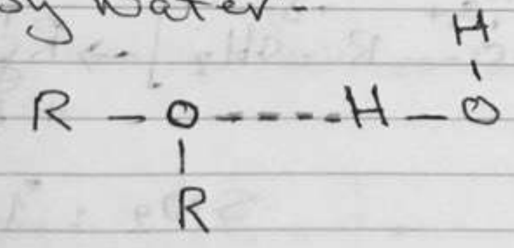
If the two groups are identical, the ether is said to be symmetrical (e.g. diethyl ether, di iso-propyl ether); if different, unsymmetrical (e.g. tert-butyl Methyl ether

$CH_3-O-C(CH_3)_2-CH_3$

physical properties of ethers :-

This weak polarity does not appreciably affect the boiling point of ethers, which are about the same as those of alkanes having comparable molecular weights, and much lower than those of isomeric alcohols. Compare, for example, the boiling point of n-heptane (98°c), methyl n-pentyl ether (100°c), and n-hexyl alcohol (157°c) - The hydrogen bonding that holds alcohol molecules strongly together is not possible for ethers, since they contain hydrogen bonded only to carbon.

On the other hand, ethers show a solubility in water comparable to that of the alcohols, both diethyl ether and n-butyl alcohol, for example, being soluble to the extent of about 8g per 100g water. We attributed the water solubility of the lower alcohols to hydrogen bonding between water molecules and alcohol molecules. The water solubility of ethers arises in the same way: through the unshared electron pairs on oxygen. ether can accept hydrogen bonds provided by water.



* Industrial sources of ethers. Dehydration of alcohols

$$2\,R-OH \xrightarrow{H_2SO_4,\ \Delta} R-O-R + H_2O$$

These ethers are prepared by reactions of the corresponding alcohols with sulfuric acid. Since molecule of water is lost for every pair of alcohol molecules, the reaction is a kind of dehydration.

As we shall soon see, alcohols can undergo another kind of dehydration, involving elimination, to give alkenes. Dehydration to ethers rather than alkenes is controlled by the choice of reaction conditions.

Ether formation by dehydration is an example of nucleophilic substitution with alcohol playing two roles: the protonated alcohol is the substrate, and the second molecule of alcohol is the nucleophile. Reaction could be either S_N1 or S_N2, depending upon whether the protonated alcohol loses water before, or simultaneously (الوقت ذاته) with, attack by the second alcohol molecule.

$$R-OH + H^+ \rightleftharpoons R-OH_2^+$$

$$R-OH_2^+ \xrightarrow{-H_2O} R^+ \xrightarrow{ROH} R-\overset{H}{\underset{\oplus}{O}}-R \rightleftharpoons H^+ + RO-R$$

S_N1: 3° and 2° alcohol

$$R-OH_2^+ \xrightarrow{ROH} \left[R-\overset{H}{O}{}^{\delta+} \cdots R \cdots \overset{\delta+}{O}H_2 \right] \rightarrow R-\overset{H}{\underset{\oplus}{O}}-R + H_2O \rightleftharpoons H^+ + ROR$$

S_N2: 1° alcohols

preparation of ethers :-

1- Williamson Synthesis

$R-X + R'O^{\ominus} Na^{\oplus} \longrightarrow R-OR' + X^-$

substrate Nucleophile

X⁻ → leaving group

yield from RX = $CH_3 > 1° > 2° (\ddot{>} 3°)$

examples :-

$CH_3-CH(CH_3)O-H \xrightarrow{Na} (CH_3)_2CH\bar{O}\overset{+}{Na} + CH_3CH_2CH_2Br$

sod- isopropoxide n-propyl Bromide

↓

$CH_3CH_2CH_2O-CH(CH_3)_2$

Isopropyl n-propyl ether

2- Alkoxymercuration -demercuration

$>C=C< + ROH + Hg(OOCCF_3)_2 \longrightarrow -\underset{RO}{C}-\underset{HgOOCCF_3}{C}-$

Alkene Mercuric trifluoroacetate

$\xrightarrow{NaBH_4} -\underset{RO}{C}-\underset{H}{C}-$

Markovnikov orientation

$CH_2=CH(CH_2)_3CH_3 \xrightarrow[(CH_3)_2CHOH \text{ solvent}]{Hg(OAc)_2} \underset{HgOAC}{CH_2}-\underset{OCH(CH_2)_3}{CH}-(CH_2)_3CH_3$

$\xrightarrow{NaBH_4}$ sod- brohydride

$\underset{H}{CH_2}-\underset{OCH(CH_2)_3}{CH}(CH_2)_3CH_3$

2-Isopropoxy hexane

* Reactions of ethers cleavage by acids

$$R-O-R' + HX \longrightarrow R-X + R'-OH \xrightarrow{HX} R'-X$$

Reactivity of HX = HI > HBr > HCl

Ethers are comparatively unreactive compounds. The ether linkage is quite stable toward bases, oxidizing agents, and reducing agent. In so far as the ether linkage itself is concerned, ethers undergo just one kind of reaction, cleavage by acids:

Cleavage takes place only under quite vigorous condition concentrated acids (usually HI or HBr) and ↑temperatures. A dialkyl ether yields initially an alkyl halides and an alcohol; the alcohol may react further to form a second mole of alkyl halide:- for example

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-O-\overset{CH_3}{\overset{|}{C}H}-CH_3 \xrightarrow[130-140^\circ C]{48\%\ HBr} 2\ CH_3-\overset{CH_3}{\overset{|}{C}H}-Br$$

diisopropyl ether — Isopropyl Bromide

تتفاعل الايثرات مع الاحماض المعدنية القوية المركزة مثل H_2SO_4 ، HI ، HBr حيث تتكسر الروابط الايثرية وتفيد مقدرة حمض HBr ، HI على كسر الروابط الإيثرية لان أيوني البروم واليود نيكلوفيلي افضل من ايون الكلور بسبب الحجم.

$$R-\ddot{O}-R' + HX \rightleftharpoons R-\overset{H}{\overset{|}{\underset{\oplus}{O}}}-R' + X^- \xrightarrow[\text{or } S_N2]{S_N1} R-X + R'-OH$$

weak base, good leaving group

* S_N1 Mechanism

① $$R-\overset{H}{\overset{|}{\underset{\oplus}{O}}}-R' \xrightarrow{\text{slow}} R^+ + HOR'$$

② $$R^+ + X^- \xrightarrow{\text{fast}} R-X$$

* or by an S_N2 Mechanism — S_N2

$$R-\overset{H}{\overset{|}{\underset{\oplus}{O}}}-R' + X^- \longrightarrow \left[\overset{\delta-}{X}\cdots R-\overset{H}{\overset{|}{\underset{\delta+}{O}}}-R'\right] \longrightarrow R-X + HOR'$$

* depending upon conditions and the structure of the ether