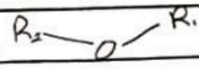
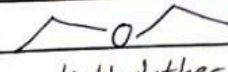
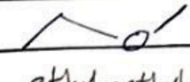
١٧ جمادى الأولى ١٤٤٣هـ   كيمياء العضوية ١٨   الوحدة ١
٢١ / ١٢ / ٢٠٢١م   د. محمد الأشرم ٢٩

Subject: Ethers

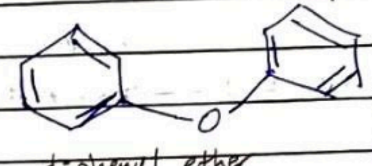
open chain ether:- 


diethylether (symmetrical)

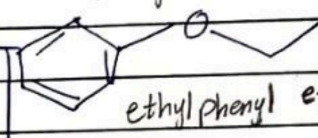

ethylmethylether (unsymmetrical)

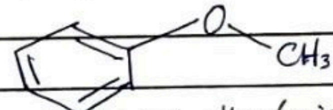
$R_1 = R_2$ = alkyl: symmetrical
$(R_1 \neq R_2)$ = alkyl: unsymmetrical
(unsymmetrical) → Ar—O—R
Ar₁—O—Ar₂

$Ar_1 = Ar_2$ ⟹ symmetrical
$Ar_1 \neq Ar_2$ ⟹ unsymmetrical

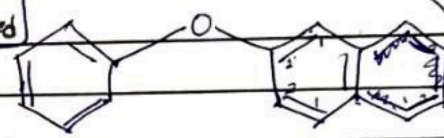

diphenyl ether

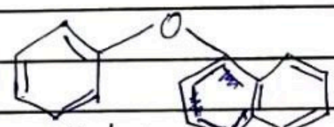
in symmetrical ethers we can exclude the prefix (di) from the name


ethylphenyl ether


methylphenyl ether (anisole)

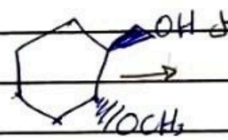
In ethers O is sp_3 hybridized

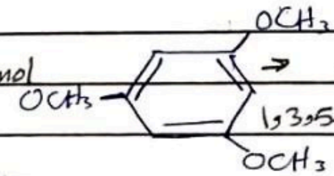

2-nepthylphenylether


1-naphthyl phenyl ether

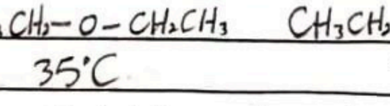
في حالة أن أطراف مجموعة الإيثر، أحدها كبير جداً مقارنة بالمجموعة الأخرى، نعتبر الأكبر مع مجموعة الألكيل الصغيرة مجموعة ألكوكسي.

$CH_3\underset{|}{C}HCH_2CH_2CH_3$
OCH_3
2-methoxypentane


مجموعة الهيدروكسيل ← أهم من الإيثر
trans-2-methoxycyclohexanol


→ في حالة وجود أكثر من مجموعة إيثر نسميهم مجموعات ألكوكسي
1,3,5-trimethoxy benzene

$CH_3CH_2O\overset{CH_3}{\overset{|}{C}}HCH(CH_3)_2$
2-ethoxy-3-methylbutane


Phenyl-n-propylether

مجموعة الألكوكسي ليس لديها أي أولوية في الترقيم

Physical properties of ethers:-

1. colorless
2. bp similar to alkane and lower than alcohol.

	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2-O-CH_2CH_3$	$CH_3CH_2-CH_2-CH_2CH_3$
b.p	118°C	35°C	36°C

3. ethers can form H-bonds with alcohols, so they dissolve each other. (They are miscible in each other)

▸ Subject: Ethers

4 ethers are generally inert, so they are used as solvents for organic compound.

5 Ethers are soluble in water, just like alcohols.

6 When ethers are exposed to air for a long time, they form peroxides which are explosive.

$CH_3CH_2\ddot{O}CH_2CH_3 + O_2 \longrightarrow CH_3CH_2OCHCH_3$ (OOH) ether hydroperoxide

Most common solvents for organic compounds are:-
1 diethyl ether
2 tetrahydrofuran THF

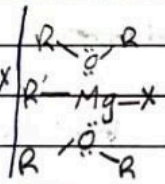
Grignard reagent organometallic compound.

$R^+-X^- + Mg \xrightarrow[\text{solvent}]{\text{dry ether}} R^--Mg^+X$ alkyl magnesium halide

* We use a dry ether as a solvent (dehydrated), to avoid destroying the grignard reagent, because R^- can accept H^+ from H_2O.

* Ethers are used in the proccess of forming grignard reagent, because it stabilizes its structure.

$R-MgX + H_2O \rightarrow R-H + Mg(OH)X$ in the case of hydrated.



$CH_3I + Mg \xrightarrow{\text{ether}} CH_3MgI$ methylmagnesium iodide

* Alkyl halides can be converted into alkanes by altering alkyl halide to grignard reagent then to alkane.

* How to prepare CH_3CHDCH_3 from $CH_2=CHCH_3$?

$CH_2=CHCH_3 \xrightarrow{HBr} CH_3CHCH_3 \xrightarrow[\text{ether}]{Mg} CH_3CHCH_3 \xrightarrow{D_2O} CH_3CHDCH_3$

alkene → alkyl halide (Br) → grignard reagent ($MgBr$) → alkane

alkyllithium:- $R-Li$ $\quad R-X + 2Li \longrightarrow R^-Li^+ + LiX$

* Alkyllithium is similar to grignard reagent in the charge of R group.

* Alkyllithium has chemical properties similar to those of grignard reagent.

~~How to~~ Preperation of ethers:-

1 alcohol + alcohol $\xrightarrow[140°C]{H_2SO_4}$ symmetrical ether + H_2O

$CH_3CH_2OH + CH_3CH_2OH \xrightarrow[\text{heat}]{H^+} CH_3CH_2OCH_2CH_3 + H_2O$

Subject : Ethers

[2] alcohol + alkene $\xrightarrow{H^+}$ ether

$CH_3OH + CH_2=C(CH_3)_2 \xrightarrow{H^+} CH_3O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$ t-butyl methyl ether

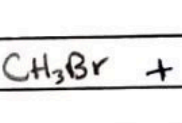
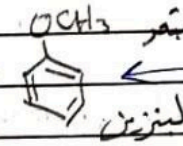
2-methyl-2-methoxy propane.

[3] Williamson synthesis for unsymmetrical ethers.

or $2ROH + 2Na \longrightarrow 2RONa + H_2$

$ROH + NaNH_2 \longrightarrow RONa + NH_3$ } first step to form alkoxide.

$RONa + R'X \longrightarrow ROR' + NaX$ second step in S_N2 mechanism, R'X is primary.

$CH_3Br +$  $\longrightarrow$  $+ CH_3O$

$CH_3Br + OCH_2(CH_3)_3 \longrightarrow CH_3OCH_2(CH_3)_3 + BrCH_2(CH_3)_3 + CH_3O$

Ether reactions:-

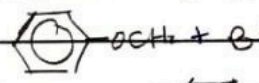
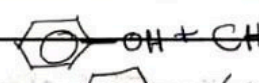
[1] cleavage of ethers

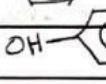
In cleavage of ethers, the nucleophile prefers the alkyl group with less branches

$R-O-R' + HI$ (strong acid) $\xrightarrow{heat} R-\overset{+}{O}(H)-R' \longrightarrow R-OH + R'I$

$R-O-R' + BBr_3$ (lewis acid) $\xrightarrow{heat}$ $R-\overset{+}{O}(BBr_3^-)-R' \longrightarrow ROH + RBr + B(OH)Br_2$

$CH_3CH_2OCH(CH_3)_2 + HI \xrightarrow{heat} CH_3CH_2I + (CH_3)_2CHOH$ S_N2

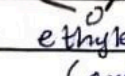
 $\xrightarrow[water]{heat}$  $+ CH_3Br + B(OH)Br_2$ most common.

$(CH_3)_3CO-$  $\xrightarrow[H_2O]{H_2SO_4, H^+}$  $+ (CH_3)_3COH$ S_N1 and $(CH_3)_2C=CH_2$ E1

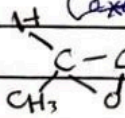
Epoxides (oxiranes)

→ it is three membered ring cyclic ether.

2-chloro oxirane



ethylene oxide (oxirane)



trans-2,3-dimethyl oxirane.

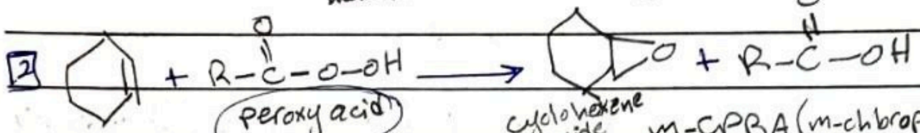
١٩ جمادى الأولى ١٤٤٣هـ   كيمياء عضوية ١٩   الوحدة ١٨

Subject: Ethers   د. محمد الأشرم ٢٠   ٢٣ / ١٢ / ٢٠٢١م

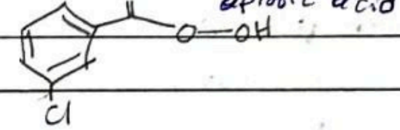
Preparing oxirane:-

[1] $CH_2{=}CH_2 + O_2 \xrightarrow[\text{heat, pressure}]{\text{silver catalyst}} CH_2{-}CH_2$ (O)

[2]



peroxy acid → the most common is m-CPBA (m-chloroperbenzoic acid) aprotic acid; cyclohexene oxide



Reactions of epoxide:- (addition reactions)

* Epoxides are much more reactive than ordinary ethers, because of the strain in the three membered ring.

note:- we use an acid catalyst, for protonation the oxirane so making it instable.

[1] reaction with water

$+ H{-}OH \xrightarrow{H^+} CH_2{-}CH_2$ (OH, OH) ethylene glycol

[2] reaction with nucleophile

$\xrightarrow{H^+}$ $\xrightarrow{CH_3OH}$ $HOCH_2CH_2OCH_3$

$\xrightarrow{OHCH_2CH_2OH}$ $HOCH_2CH_2OCH_2CH_2OH$

As they are weak nucleophiles, we need an acid catalyst.

[3] reaction with grignard or alkyllithium.

(ways for preparing alcohols)

$R{-}MgX + H_2C{-}CH_2$ (O) $\rightarrow RCH_2CH_2OMgX \xrightarrow{H_2O} RCH_2CH_2OH + Mg(OH)X$

$R^-{-}Li^+ +$ (O) $\rightarrow RCH_2CH_2OLi \xrightarrow{H_2O} RCH_2CH_2OH + LiOH$

$C_6H_5CH_2MgBr +$ (O) $\xrightarrow{H_2O} C_6H_5CH_2CH_2CH_2OH$

$CH_3C{\equiv}C^-Na^+ +$ (O) $\xrightarrow{H_2O} CH_3C{\equiv}CCH_2CH_2OH$

وضح خطوات * تكوين $CH_3CH{=}CHCH_2CH_3$ من $BrCH_2C{\equiv}CCH_2CH_3$

[1] تفاعل الألكاين مع H_2 لينتج $BrCH_2CH{=}CHCH_2CH_3$

[2] تفاعله مع Mg بوجود إيثر $BrMgCH_2CH{=}CHCH_2CH_3$

[3] تفاعله مع H_2O لتحطيم المركب $Mg(OH)Br + CH_3CH{=}CHCH_2CH_3$