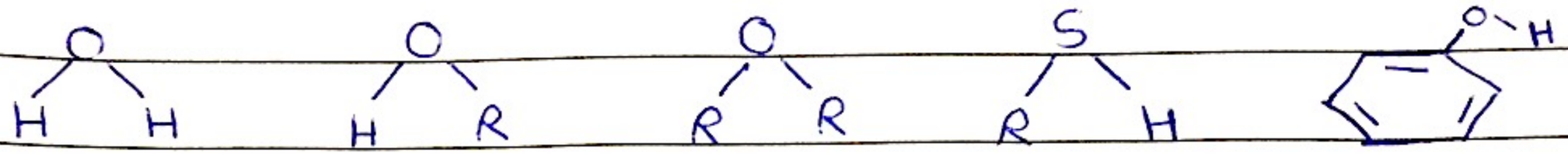
Subject Date No.

Chapter 7 : Alcohols, phenols and thiols



water alcohol ether thiol phenol

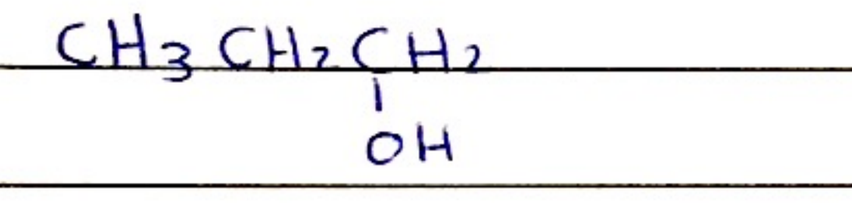
7.1 : Nomenclature of Alcohol

CH_3OH CH_3CH_2OH

Methanol ethanol

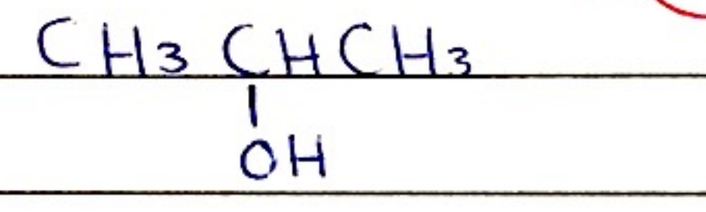
(Methyl alcohol) (ethyl alcohol)

* لم يتم ذكر الـ common name في المحاضرة



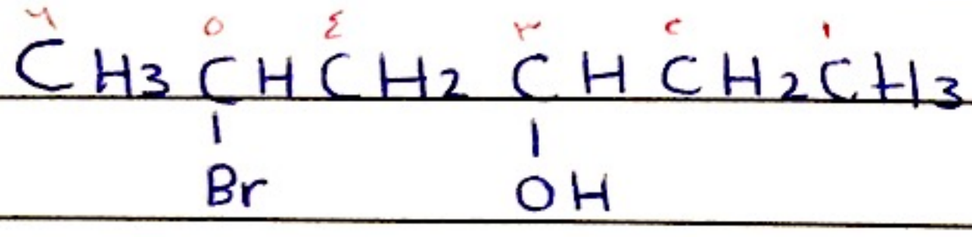
1- propanol

(n-propyl alcohol)



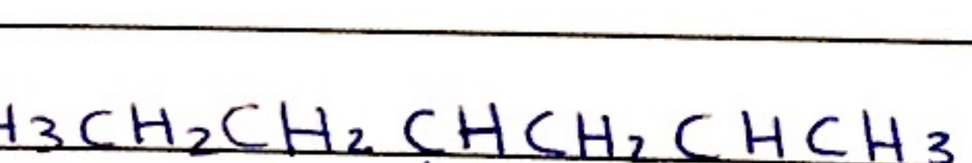
2- propanol

(isopropyl alcohol)



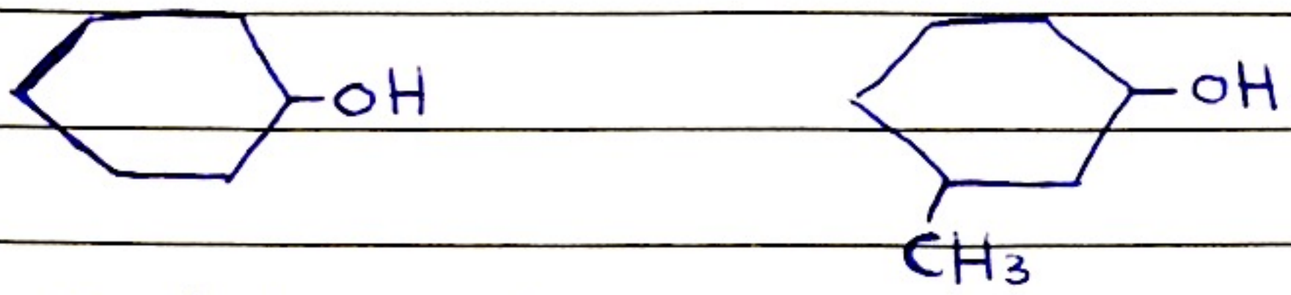
* الأولوية لمجموعة الهيدروكسيل

5- Bromo-3-hexanol



* الأولوية تعد من الجهة الأقرب لـ OH ولأنها موجودة بنص المركب تعد من الجهة الأقرب للتفرعات المتماثلة

2-bromo-4-heptanol



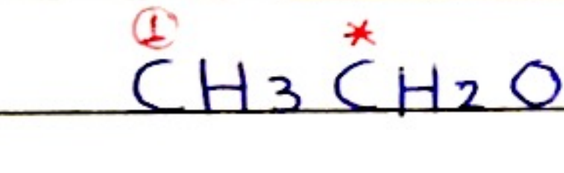
* الاولوية للـ OH وليست للرابطة الثنائية ^^

4- penten -2- ol

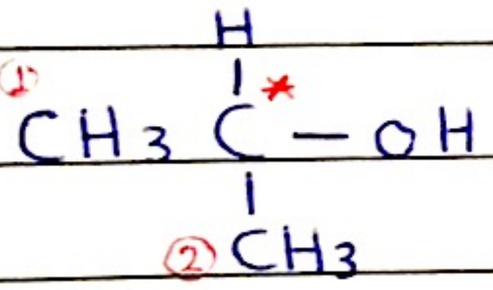
cyclohexanol

3-methyl cyclohexanol

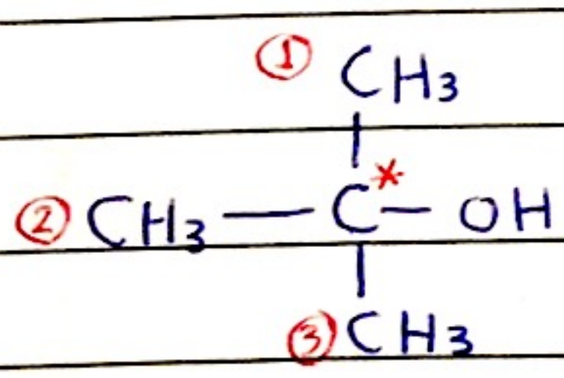
7.2 : the classification of Alcohols



primary (1°)



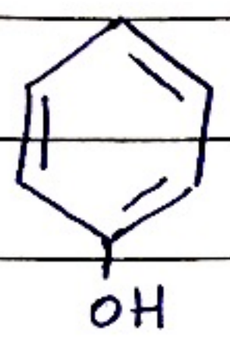
Secondary (2°)



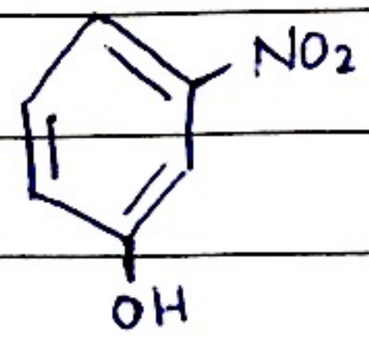
Tertiary (3°)

Subject

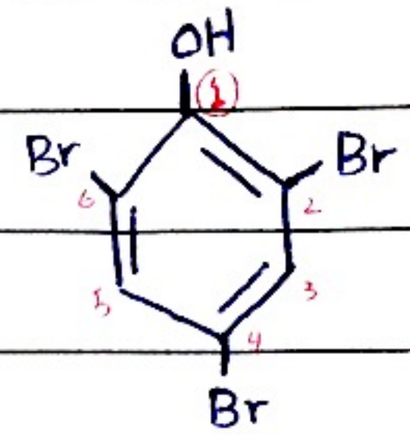
7.3 : Nomenclature of phenols



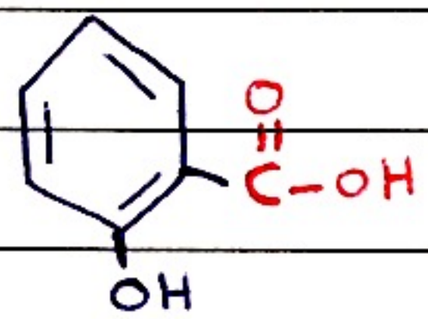
phenol



m-nitrophenol

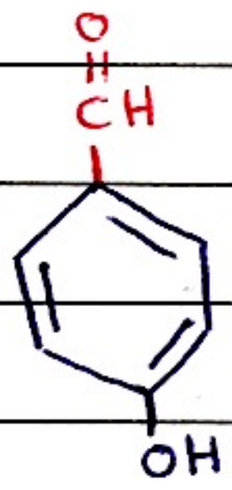


2,4,6-tribromophenol



O-hydroxy benzoic acid

** في هذه الحالة آخذ التفريعين الهم
اسم شائع لكن داعماً نعامل الـ OH كفرع ⇐
ونسميه (hydroxy) والمجموعة الثانية
نعتمدها الـ common name



p-hydroxy benzaldehyde

7.4 : Hydrogen bonding in Alcohols and phenols

* we look at the physical properties

	CH_3CH_2-OH	CH_3-O-CH_3	$CH_3CH_2CH_3$
Molecular weight	46	46	44
boiling point	+78.5	-24	-42

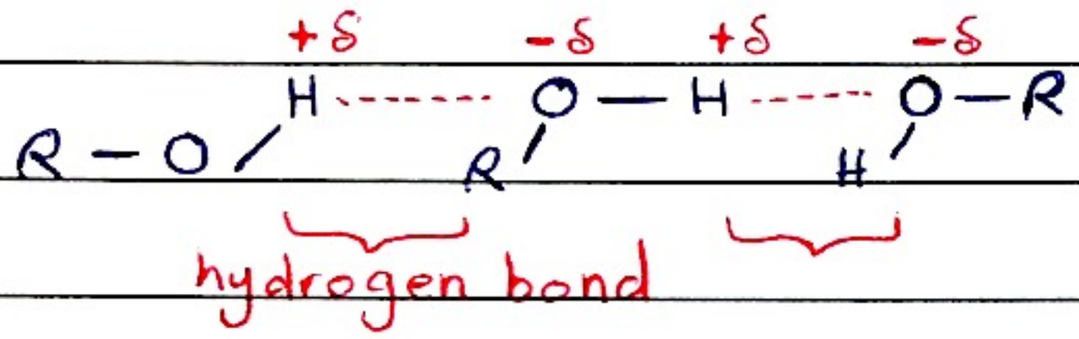
Subject Date No.

⟹ CH_3CH_2OH CH_3-O-CH_3 $CH_3CH_2CH_3$

type of bonding | hydrogen bonding | dipole – dipole | Van der Waals

↳ the strongest one

* تتكون الرابطة الهيدروجينية بين جزيئين كحول وأكثر



* high electronegativity of the oxygen atom

⟹ solubility b.p solubility

C – OH	65	Completely miscible
C – C – OH	78	Completely miscible
C – C – C – OH	97	Completely miscible
C – C – C – C – OH	117	9.7
C – C – C – C – C – OH	137	2.7
C – C – C – C – C – C – OH	157	.58

"ثلاثين أول"

* كلما زاد عدد ذرات الكربون يزداد الـ (non polar tail)
وبالتالي تقل الذائبية

Subject Date No.

7.5 : Acidity and basicity

* يتم استخدام محيطلحين او طريقتين لتعريف الحموض والقواعد :

① Bronsted - lowry

② lewis

⟹ Firstly : bronsted lowry :

$$\underset{\text{bronsted base}}{\underline{H_2O}} + \underset{\text{bronsted acid}}{\underline{HCl}} \longrightarrow \underset{\text{Conjugate acid}}{\underline{H_3O^+}} + \underset{\text{Conjugate base}}{\underline{Cl^-}}$$

* حسب مفهوم برونستد لوري :

* الحمض يمنح H^+ * والقاعدة تستقبل H^+

* اذا كان الحمض قوي فإن قاعدته المرافقة ضعيفة والعكس صحيح

- Why we said that HCl is strong acid ?

because HCl is totally ionized in water

$$\underset{\text{weak acid}}{\underline{HA}} + \underset{\text{base}}{\underline{H_2O}} \rightleftharpoons H_3O^+ + A^- \quad \text{(equilibrium reaction)}$$

* الاتزان يرجح تكوين الاضعف

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

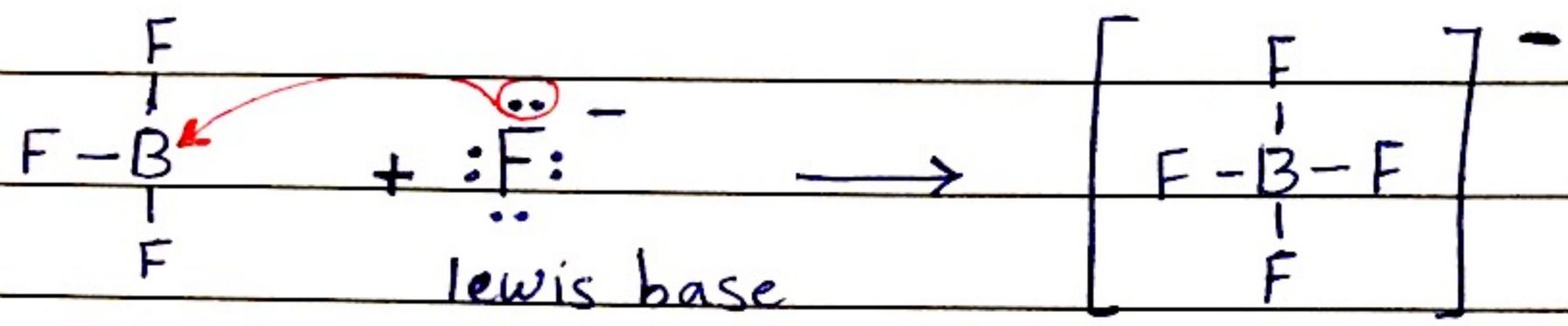
K_a : acidity Constant

** In organic, we dont like compare acid with ka . So, we use pka

* pka = −log ka ⇝ pka ↑ acidity ↓

pka ↓ acidity ↑

⟹ the second difinition of acid : lewis



lewis acid

* we dont have H^+, we have pair of electron.
* the acid will accept two electron from the base.

acid : accept the electrons

base : donate the electrons

$H_2O + NH_3 \longrightarrow NH_4^+ + OH^-$

acid base conjugate acid Conjugate base

* لما يكونه بالتفاعل حمض قوي وماء ⇐ تتفاعل كماء كقاعدة

لما يكونه بالتفاعل قاعدة قوية وماء ⇐ تتفاعل كماء كحمض

SO, water reacts as base and acid ⟹ amphoteric

Subject Date No.

7.6 : Acidity of Alcohols and phenols

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$ka = \frac{[H_3O^+][A^-]}{[HA]} \qquad pka = -\log ka$$

remember pka ↑ acidity ↓

$$R\text{-}OH + H_2O \rightleftharpoons H_3O^+ + RO^-$$

	pka
H_2O	15.7
$CH_3\text{-}OH$	15.5
CH_3CH_2OH	15.9
$CH_3\text{-}C(CH_3)_2\text{-}OH$	18

تقريباً نفس الثنتي (acidity)

* molecules like to be neutral

* كنت مقارنة بين CH_3OH و $CH_3\text{-}C(CH_3)_2\text{-}OH$

go more to the right ← to the left

pka ↓ acidity ↑ ⇐ CH_3OH

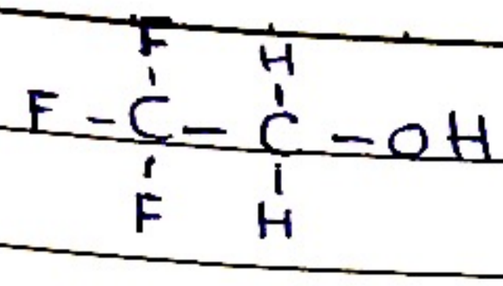
acidity of $CH_3\text{-}C(CH_3)_2\text{-}OH$ < acidity of CH_3OH

$$CH_3\text{-}C(CH_3)_2\text{-}OH + H_2O \rightleftharpoons CH_3\text{-}C(CH_3)_2\text{-}O^- + H_3O^+$$

equilibrium shift to the left to decrease the negative charge

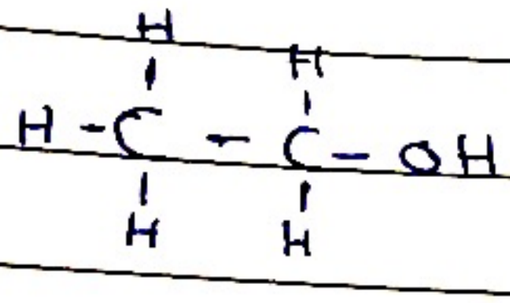
electron will increase the intensity of negative charge

Subject * more acid → more conc of H^+ Date No.



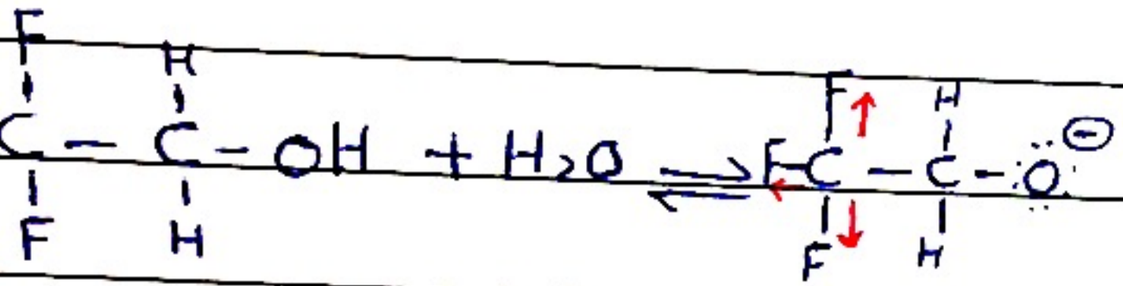
(pka = 12.4)

* F : more electronegative



(pka = 15.9) more acidity

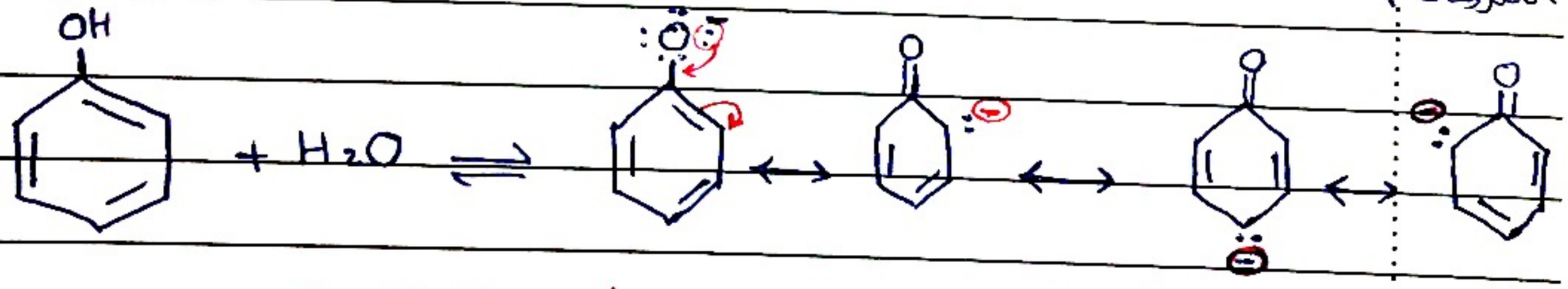
* كل ما اتجه لليمين ← more acidity



vxn go more to the right

لانه لفلور تقلل من تركيز الشحنة السالبة على الاكسجين (تسحب الالكترونات فوقها)

* phenols are more acidity than alcohols (لانها تمتلك الكترونات)



* we can draw resonance structure

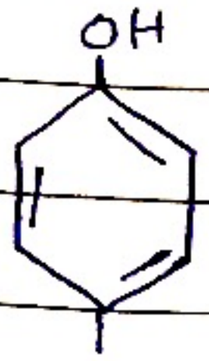
* يعني الشحنة السالبة تتوزع

the negative charge is distributed between O and C

so, the intensity of the negative charge decrease

the rxn go the right

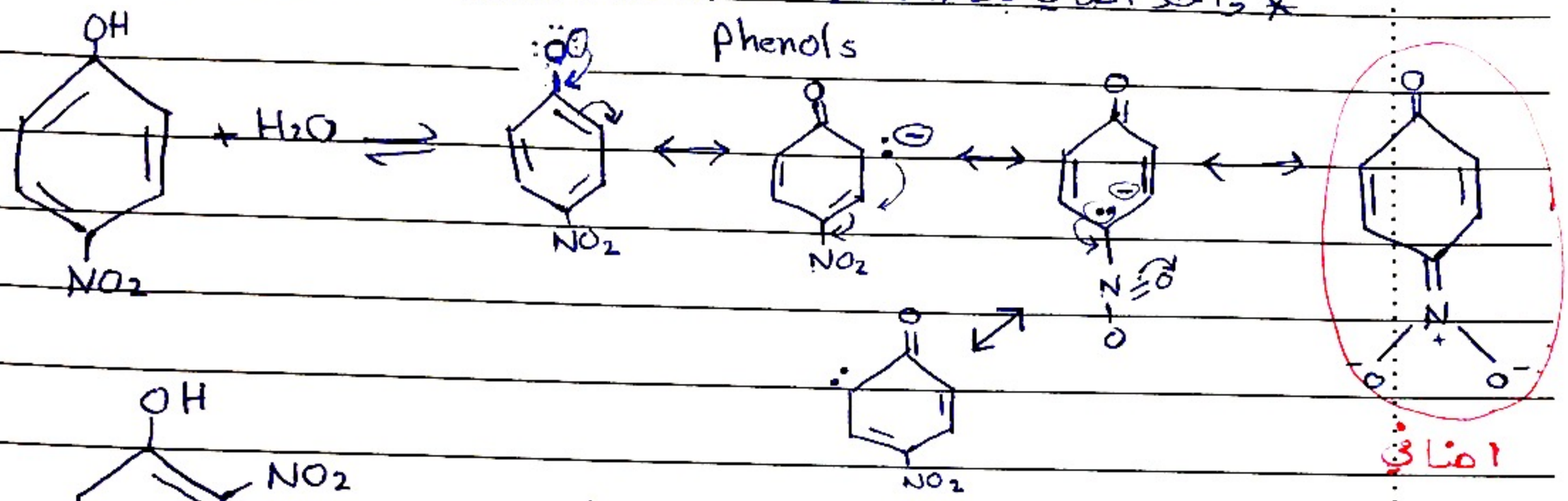
Subject Date No.



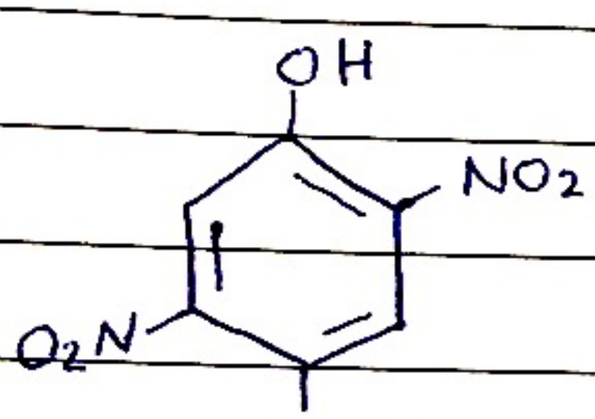
pka = 7.2

here we have another resonance structure

* واحد اضافي بالاضافة لل resonance of phenols



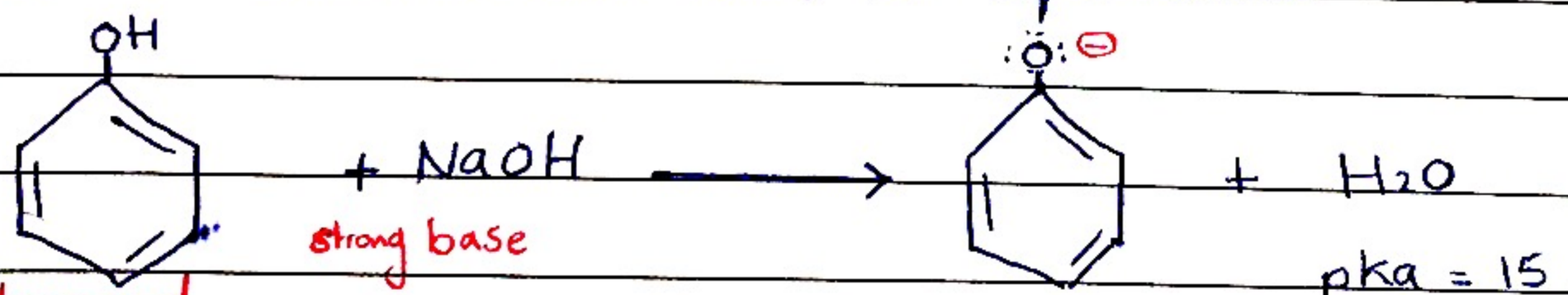
اضافي



pka = .25

* here we have more and more resonance structure than phenols

acid base reaction ⟶ no equilibrium



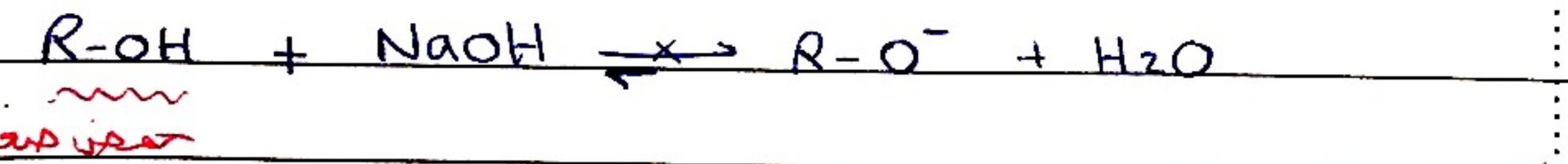
strong acid
pka = 10

strong base

peroxide ion

pka = 15

no equilibrium



حمض ضعيف

gas will leave the reaction

alkoxide ion

the rxn go to the right

RoH more acidity than H_2

Subject

Date

No.

7.7 : The basicity of Alcohols and phenols

$$R-OH + \underbrace{H^+}_{\text{From acid}} \rightleftharpoons R-\overset{\oplus}{O}\begin{matrix}H\\H\end{matrix}$$

base

* الكحول مادة امفوتيرية تتفاعل كحمض او قاعدة

7.8 reaction of Alcohols (Dehydration of alcohols to alkene)

$$CH_3-CH_2-OH \xrightarrow[180\,C^\circ]{H^+} CH_2=CH_2 + H_2O$$

From H_2SO_4 or H_3PO_4

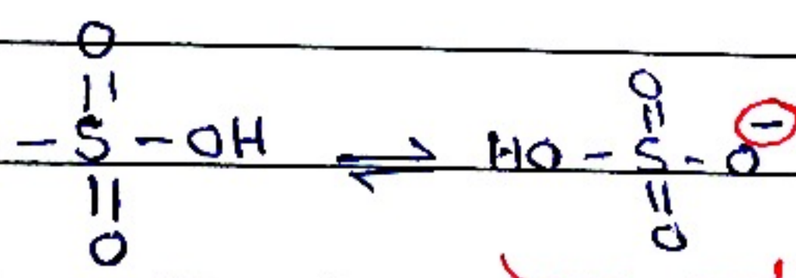
(CH_2-CH_2) (H, OH)

elemination rxn

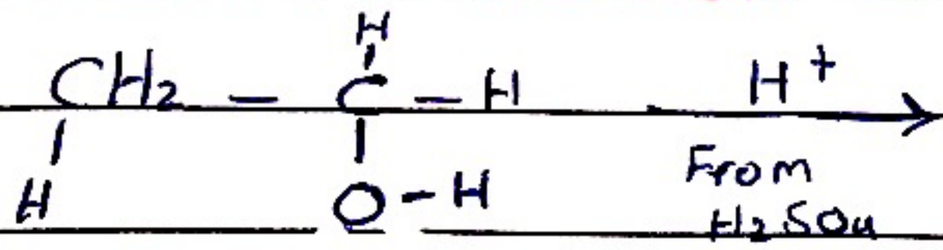
hydration : addition of water

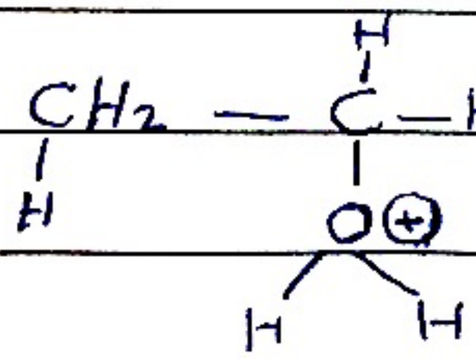
dehydration : removing of water

$H_2SO_4 \rightsquigarrow H^+$



Mechanisim of reaction





1. protonation of alcohol

* هل يحتاج لسلك

تفاعل حذف ولا

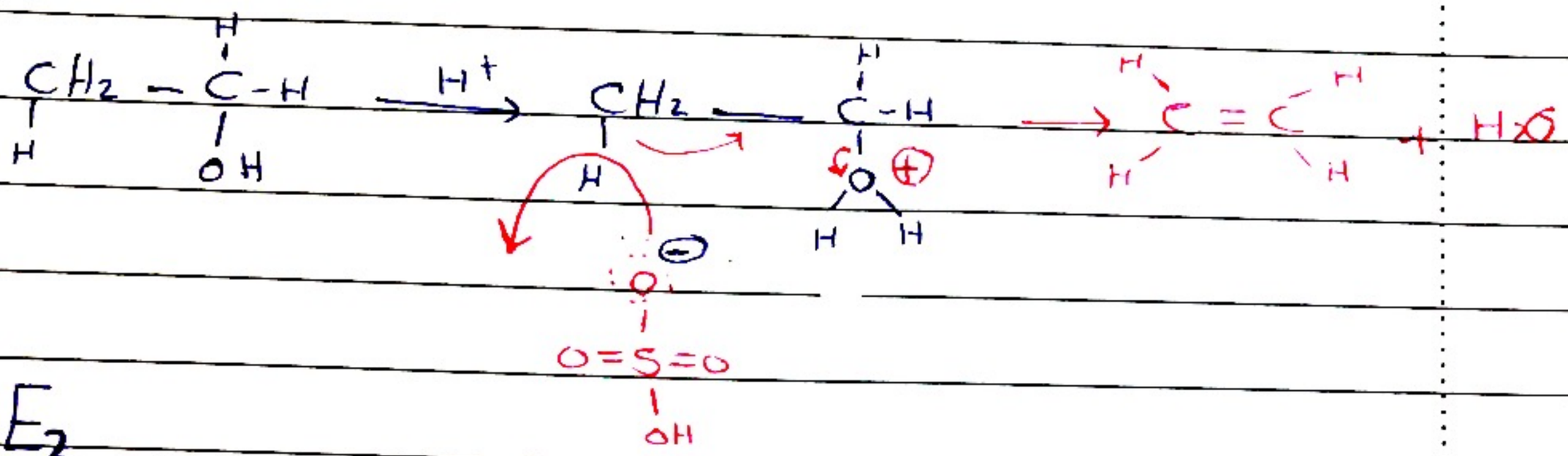
استبدال ؟!

Subject Date No.

H_2SO_4 Form resonance structure

not so strong nucleophile

لانه بشحنة سالبة بتوزع على ٣ ذرات اكسجين

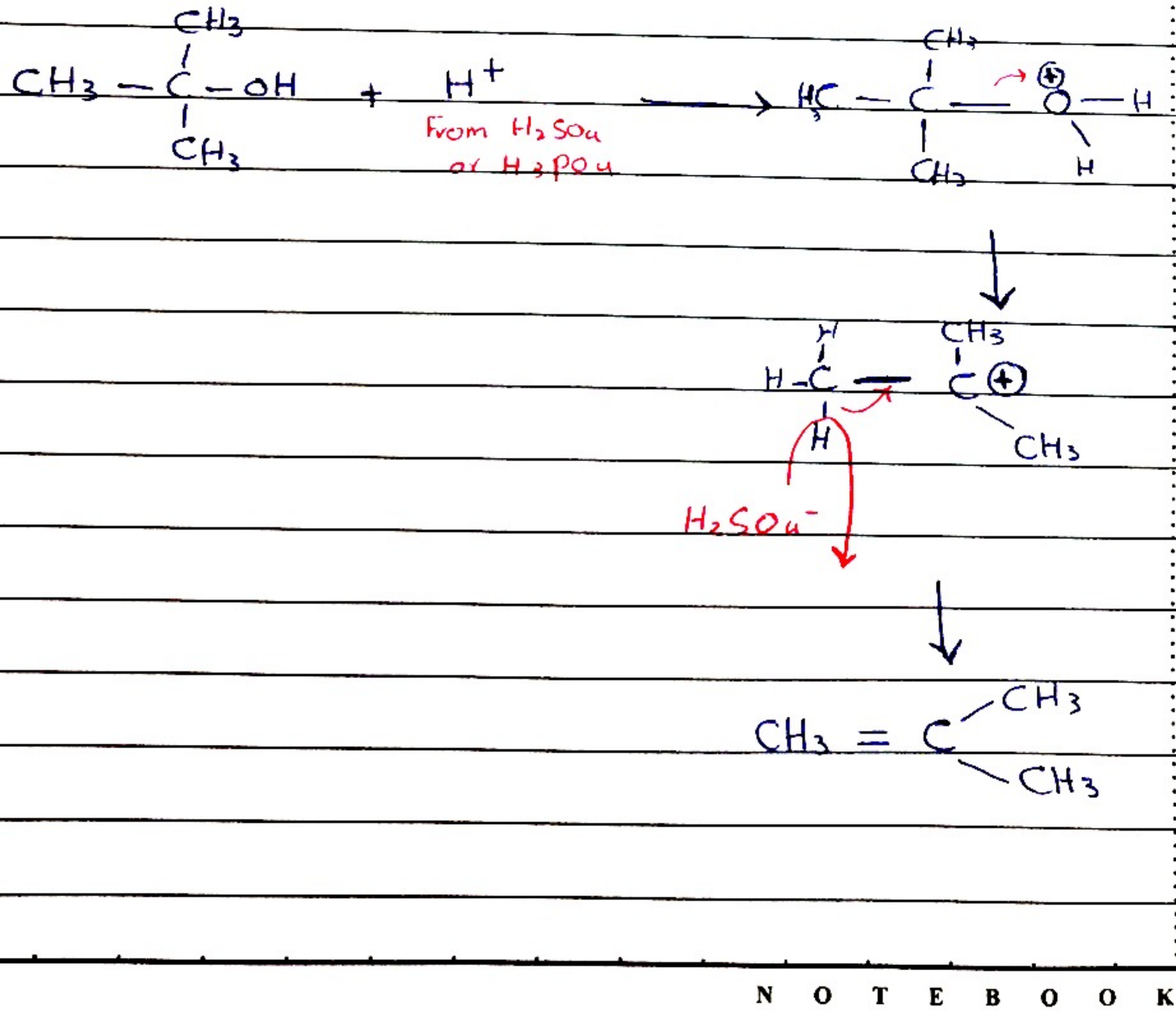


E_2

↓

١° لانه الكحول

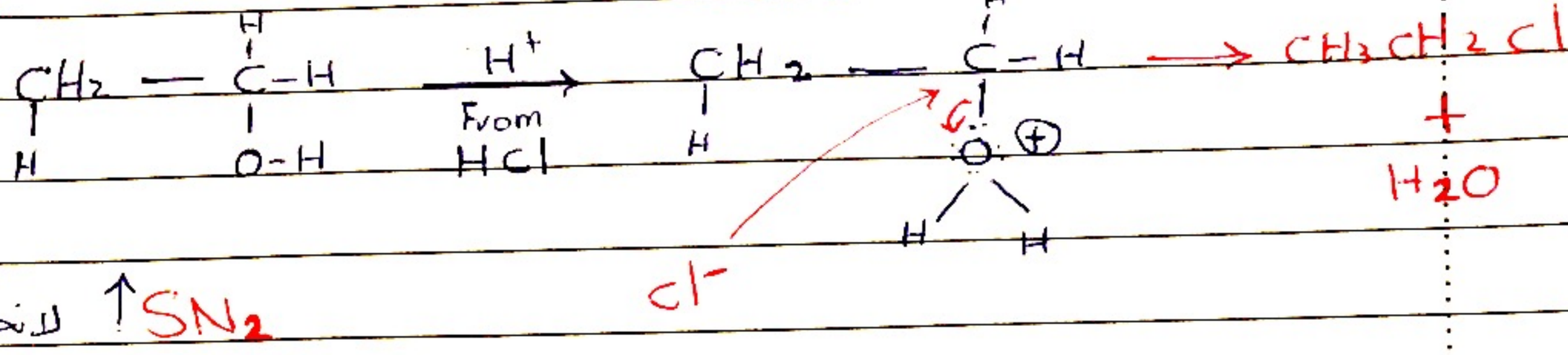
another example on 3° alcohol



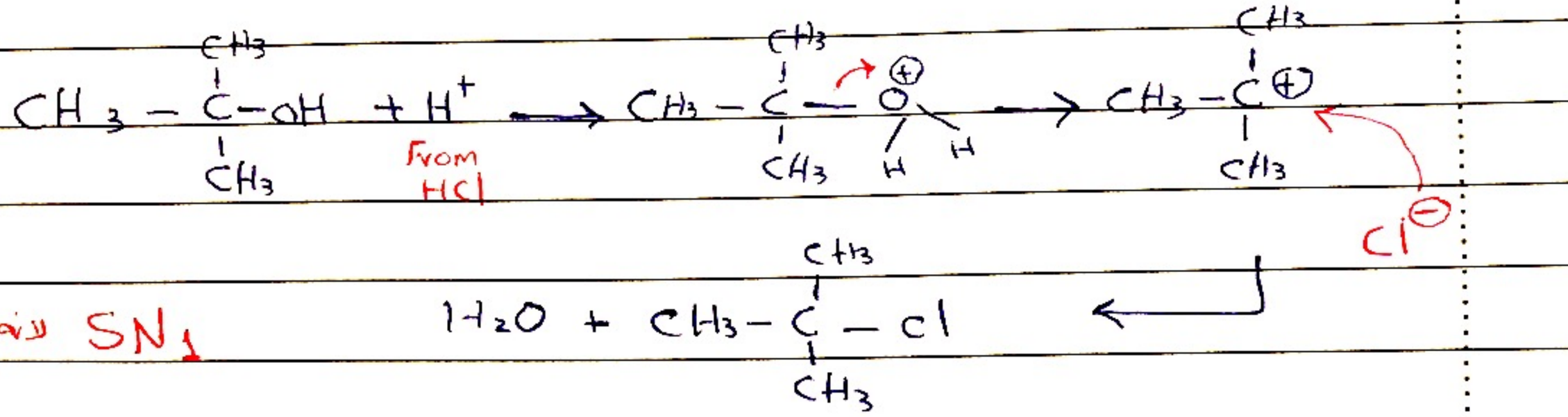
NOTEBOOK

Subject

7.9 : Reactions of alcohols with HX

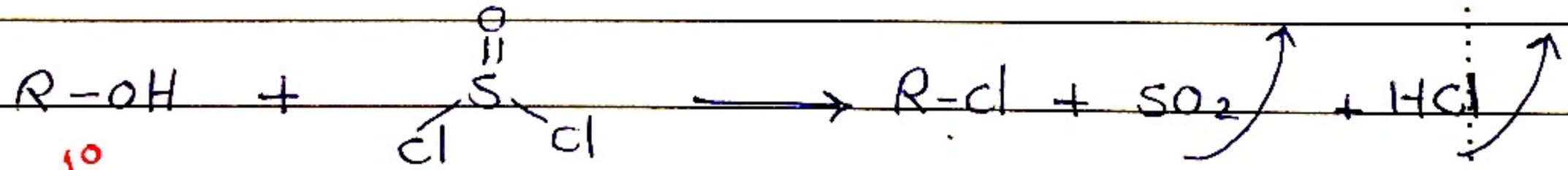


1° alcohol ↑ SN_2



7.10 : Other way to prepare alkyl halide From alcohol

(Just only substitution)



very clear rxn

لانه بطارات بتطلع

* the mechanisim isn't requiered ^^

* اي بده يدرسها بدرسها من الكتاب =-=

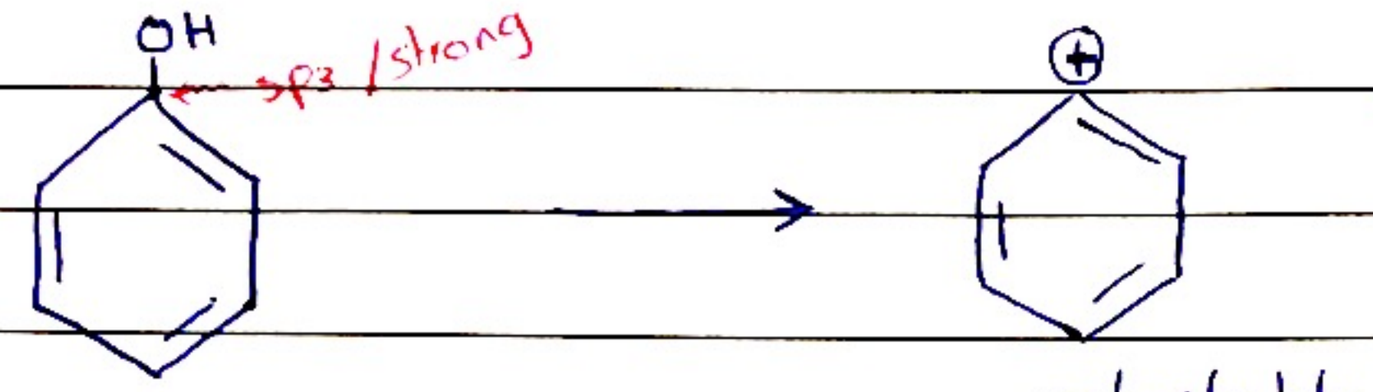
← هاي ملاحظة خصوصي من ولد الحلو

$$R\text{-}OH + PX_3 \longrightarrow R\text{-}X + H_3PO_3$$

$$PCl_3 \longrightarrow R\text{-}Cl$$

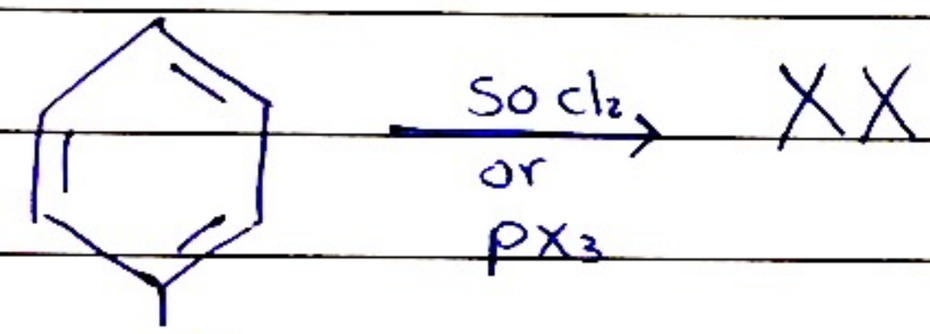
$$PBr_3 \longrightarrow R\text{-}Br$$

7.11 :



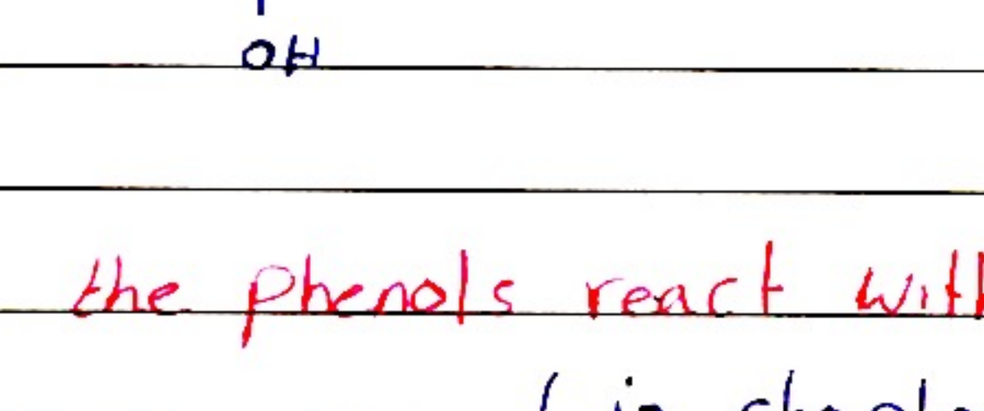
not stable

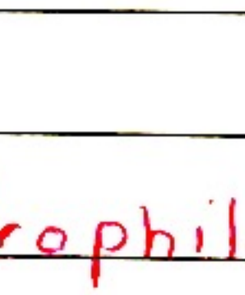
E_2 ، S_{N1} الانتقالي
E_1 S_{N2}



the phenols react with electrophile (E^+)
(in chapter 4) only

* Comparasion between alcohols and phenols





طابع بتفاعل

SN_1 X

SN_2 X

E_2 X

E_1 X

$SOCl_2$ X

PCl_3 X

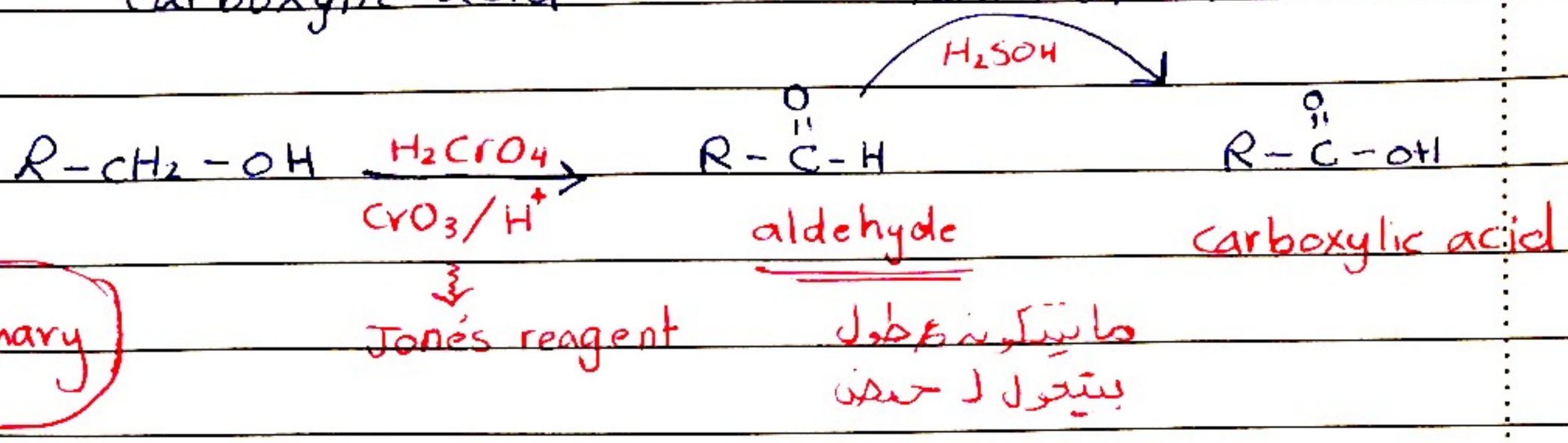
7.14 يتبع بـ

لانه عنده كثير الكترونات
يتفاعل مع النيوكليوفيل
SN_2 X

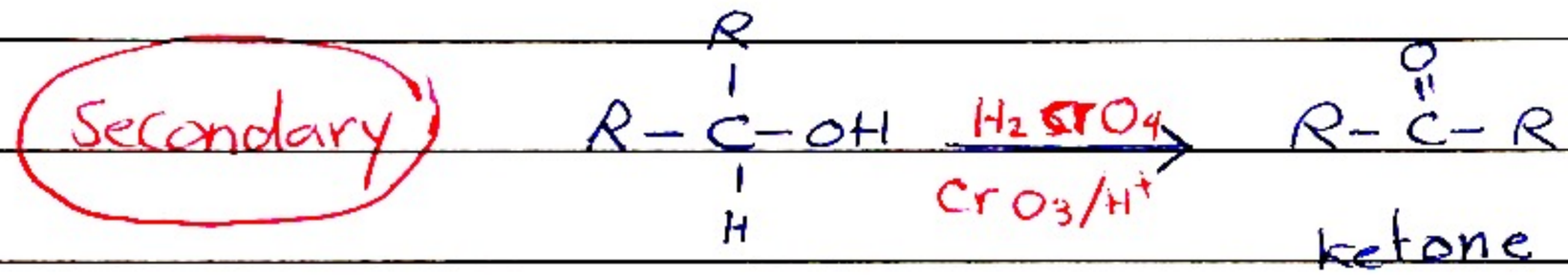
طابع بتفاعل SN_1 لانه
عنده مجموعة
مرجبة
او كهربي غير مستقر

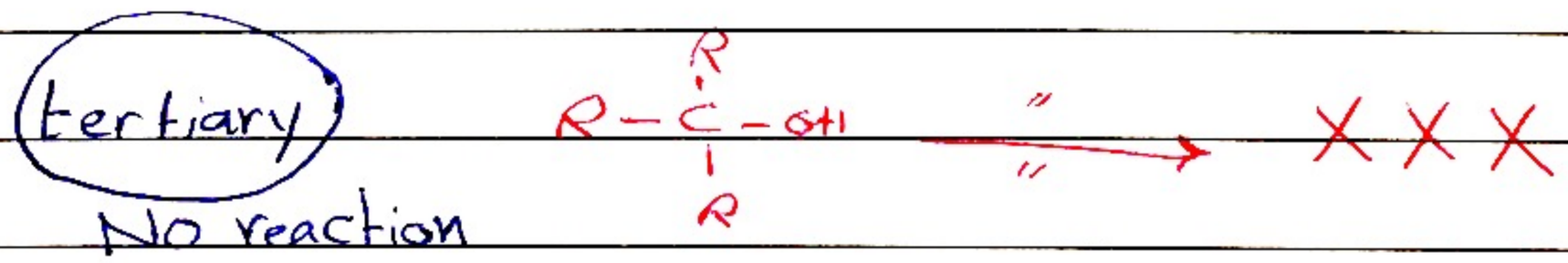
Subject Date No.

7.12 : oxidation of alcohols to aldehydes and carboxylic acid



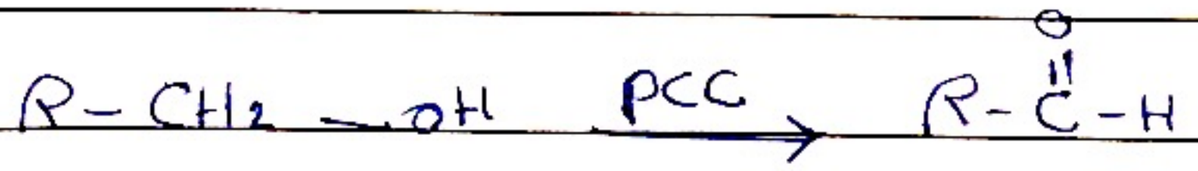
the aldehyde is very active and continued to produce the carboxylic acid

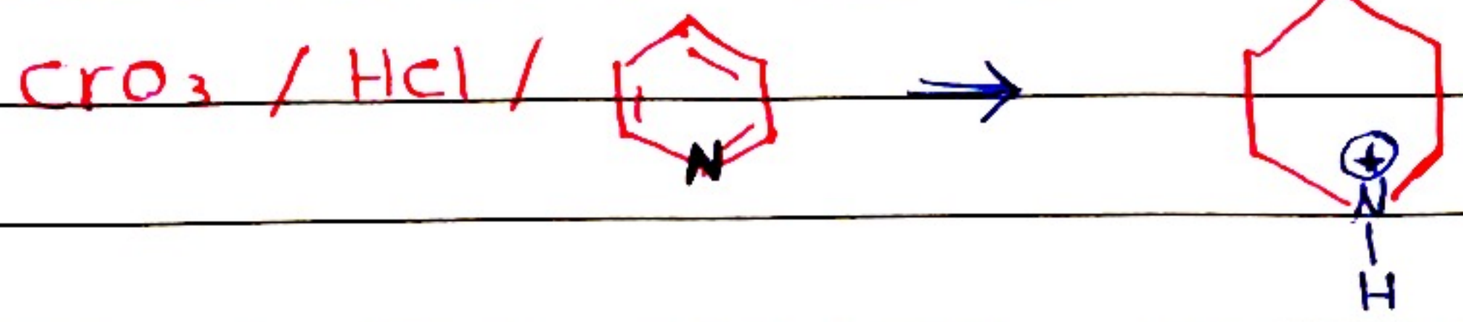




there is a problem : we need to produce aldehyde

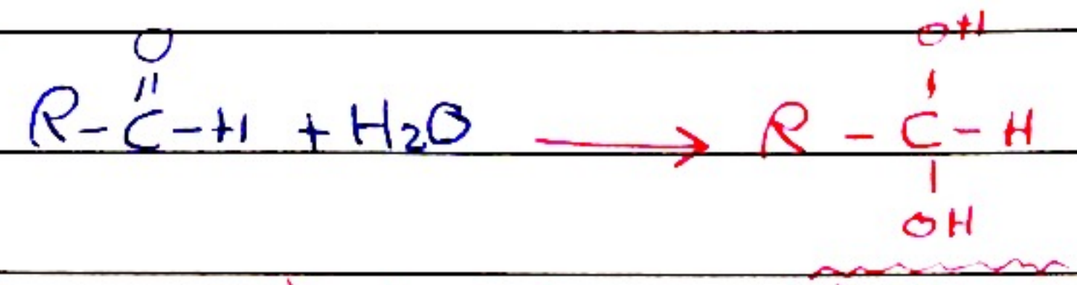
↳ We use another reagent





pyridinium chloro chromate

* إذا لا يوجد ماء مع بنزول لحمض



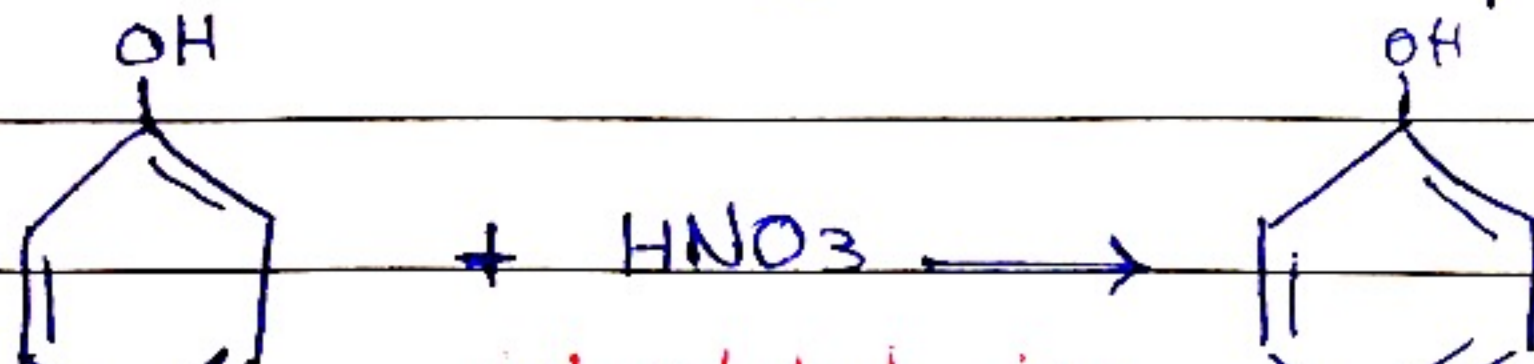
hydrate

بسرعة التأكسد لـ حمض كربوكسيلي

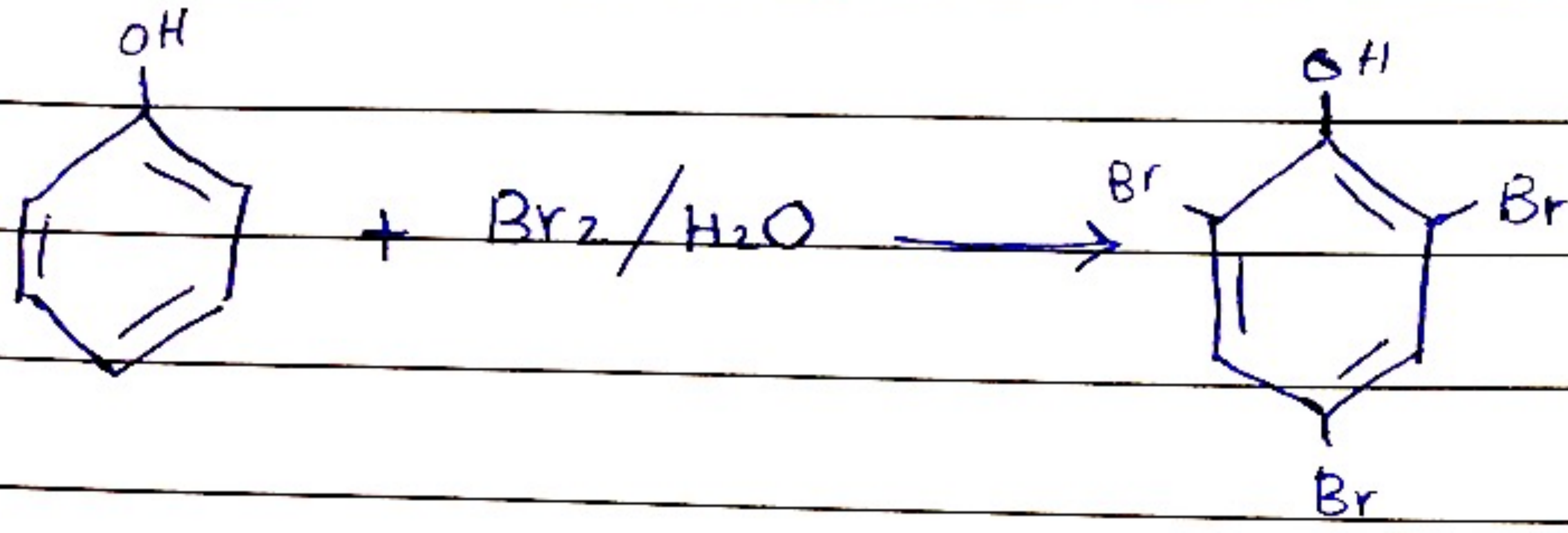
* أما بوجود PCC ← ماني ماء لهيك
ما بيتأكسد لحمض كربوكسيلي

7.13
7.15
7.16
} Not include

7.14 : aromatic substitution in phenols



ما في catalyst لأنه
الفينول نشيط كتير ولا يحتاج للتفاعل



phenols are very active group and they don't need a catalyst

7.17 : thiols

* نفس التسمية بالكحول لكن بدل

thiol ⟵ ol

CH_3-SH

methanthiol

C − C − C − C
        |
       SH

2-butanthiol

Subject Date No.

acidity of thiols

7.17 تابع → R–SH pKa 10

$$R-S-H + NaOH \longrightarrow R-\ddot{S}:^{\ominus} + H_2O$$

$$R-O-H + NaOH \rightleftharpoons R-O^{\ominus} + H_2O$$

go to the left

R-S-H is stronger acid than R-OH

So, $R-O^-$ is strong base than $R-S^-$

$$R-OH + Na \longrightarrow R-O^- + H_2O$$

$$* \quad R-X + HS^- \longrightarrow R-S-H$$

substitution reaction

* تفاعل مهم جدًا ←

$$2\ R-SH \xrightarrow{\text{oxidation}} R-S-S-R$$

$$\xleftarrow{\text{Reduction}}$$

oxidation reagent H_2O_2