Organic Chemistry One.

*** Course Summary ***

Student: **Marah Isam Falit**

Lecturer: **Prof. Usama Abu-mohsen**

Semester: **Second Semester of the year 2019/2020**

alazharpharmacy.com

• **organic chemistry :**

Branch of chemistry concerned with studying chemical compound containing carbon and hydrogen.

chemical compound

organic (from ↓ animal, vegetable)

inorganic ↓ Minerd

$_{6}C^{12}$: $1s^2$ $2s^2$ $2p^2$ — group No. 4, period No. 2

four grou

• **bond :** Attraction force between atoms that linked in the compound.

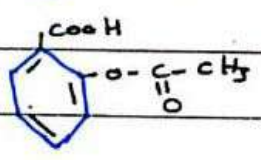
Types of chemical Bonds

Ionic covalent metalic.

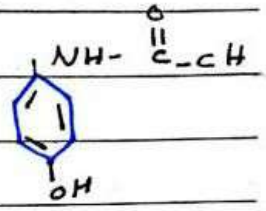
• **Ionic bond :** completely transfare of electron from atom to another.

metal + non metal → E.N 7, 1, 7

• Most drugs contain C, H



Asprine



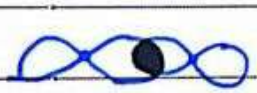
Paracetamol

• **Covalent bond :-** one or more electrons shared between two atoms.

Bond order

Single C.B	double C.B	triple C.B
C : C	C :: C	C ::: C

* **Bond length :-** $C-C > C=C > C\equiv C$


σ bond.


π bond.

Sid by Sid :

Types of covalent bond C.B according to Electronegativity E.N

- Polar C.B.
- non Polar C.B.

Electronegativity :- E.N The ability of atom to gain electron toward itself.

Note :-

- If chemical compound contains only two atoms, The polarity depend on E.N.

A) If the atoms were the same, There's No dipole moment.

ex: μ = zero $\Rightarrow$ F_2 $\Rightarrow$ F — F $\mu = 0$

B) If the atoms were different.

Ex: $\mu > 0$ $\Rightarrow$ HF $\Rightarrow$ $^{+\delta}H \longrightarrow F^{-\delta}$

- Arrange the followings compounds according increasing in Polarity :- HF , NaF , F_2

$\overset{+}{Na}\overset{-}{F}$, $\overset{+\delta}{H}\overset{-\delta}{F}$, F_2 .

↓ Ionic Bond

$\mu > 0$ ↓ c.b

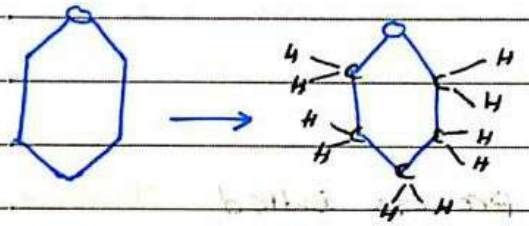
$\mu = 0$

→ increase in Polarity

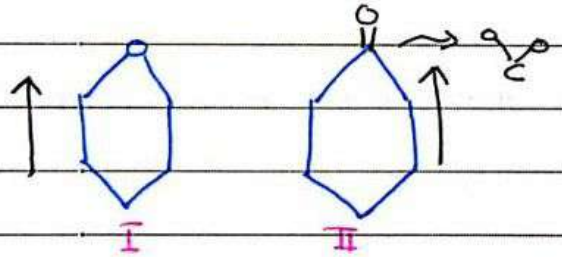
↓ decrease in Polarity .

* Direction of Polarity :- اتجاه , لقطبية يتوجه باتجاه الذرة الأكثر E.N

- E.N between C, H the same.



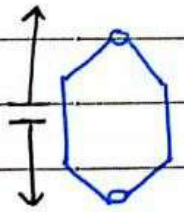
باتجاه O



I II

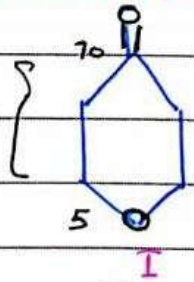
→ The same direction , but II the average of E.N is more than I

عزم قطبي أكثر



M = Zero

which is more Polar ??



I

II

N o (f) ↓ أقل كهروسالبية

C → 4 bond

O → 2

N → 3 ⇝ بالأكثر شيوعاً drugs .

I < II

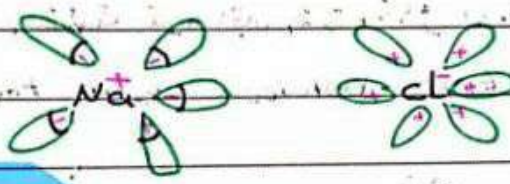
* تنخفض قوة الحمض 10 .

The relationship between Solubility and polarity ??

- **Solubility:** The interaction between solute and solvent.

- **Solvation:** description how the solute distributed among solvent without reaction occurance.

ex: NaCl in water



كيفية توزيع المذاب بين المذيب بدون تفاعل.

- If the solvent is water the process called **Hydration**

- **Solvolysis:** description how the solute react with solvent water hydrolysis.

- Ionic compound > covalent compound

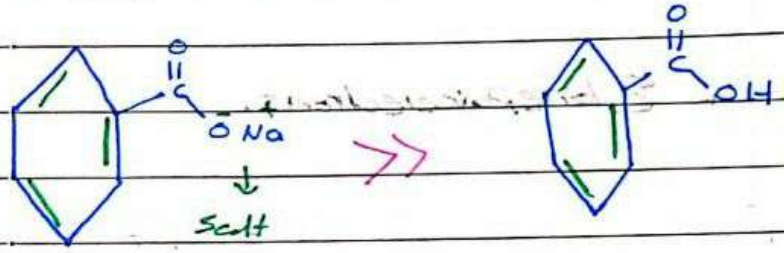
لم يذوب بشكل أكثر من Covalent.

The factors affecting on Solubility:-

1) Ionic bond +

in water ← Salt +

العامل الذي يؤثر بالذوبان :



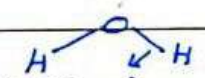
2. Hydrogen bond : H.B.

• Note :-

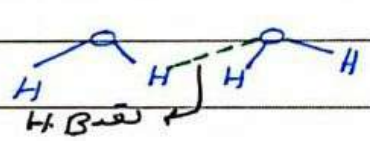
في الرابطة الهيدروجينية يكون H واقع بين ذرتين لهما كهروسالبية عالية ...

مثل: NoF بين الجزيئات يسمى

الجزئي نفسه مثل .



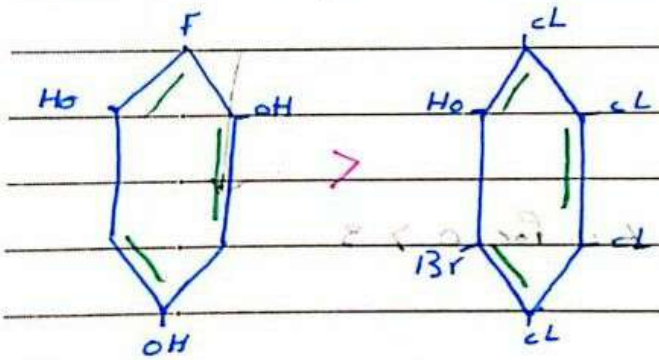
تسمى H.B



يكون

كلما زادت قدرة المركبات على تكوين روابط هيدروجينية زادت قدرتها على الذوبان أكثر بالماء .

Direct proportiration ∝

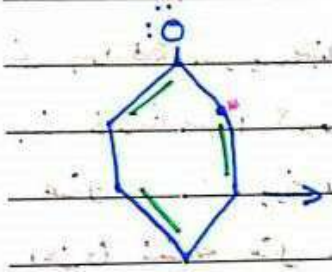


Hybridization

Depend on octet Rule ⇒ نعتبر الذرة المركزية لازم تكون مكتملة

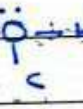
Hybridization = $\Sigma\sigma$ + Σ lonepair electrons.

CCl_4  sp^3 ، CO_2 $O \overset{\sigma}{=} C \overset{\sigma}{=} O$ sp



C ← sp^2

O ← sp^3



- في أغلب الأحيان يكون lonepair على O أو N أو S يكون بـ C ← H.

Which of the following is more polar :-

CH_3OH or CH_3SH

$CH_3OH \gg CH_3SH$, Because E.N for O > S

Acidity and basicity:

- Lewis concept:

- any substance that has empty orbital or positive charge is lewis Acid " electro phyillic" substance
هي تستقبل إلكترونات

- عناصر المجموعة الثالثة والانتقالية ما عدا الزنك دقة أصناف لويس

- any substance that has lone pair electron or negative charge is called "lewis base" " nucleo phyillic" substance.
NH_3 ، CN^- ، OH^-

- which is more Acidity.

$AlCl_3$ BCl_3

- حجم B أقل يكون جذب للنواة

↑ Acidity تكون جذب النواة لأربع إلكترون كبيرة، قوة، سحب أعلى ∴

$(CH_3)_2\ddot{O}$: $(CH_3)_2\ddot{S}$:

- كل ما كان الحجم أكبر كلما كانت قوة الجذب أقل وبالتالي تكون تسرل بفقد الإلكترونات فتزداد ↑ basicity

Acid

Strong weak

$HA \rightleftharpoons H^+ + A^-$

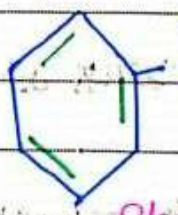
$ka = \frac{[H^+][A^-]}{[HA]}$

ka ↑ ↑ Acidity

Pka ↑ ↓ Acidity

$Pka = -\log ka$.

Arrange the following compound according increasing in their Acidity :-



, H_2O , CH_3COOH

$pK_a = 4.19$ $pK_a = 15.4$ $pK_a = 4,7$

I > III > II

Acid

binary — تكون H مرتبطة بذرة واحدة ○ — $H-X$ — HF — HCl

oxyacid — تكون H مرتبطة مجموعة به — H_2SO_4 — $HClO_4$ — HNO_3

The factors affectings on Acidity strength :-

1) E.N " period "

قدرتها الحمض تقل بفقد H قدرتها تكون

أكثر حامضية

$\overset{4}{CH_4} < \overset{5}{NH_3} < \overset{6}{H_2O} < \overset{7}{HF}$

2) size " group "

I :

$HF < HCl < HBr < HI$

F
Cl
Br
I

increasing in size

3) Hybridization

$HC \equiv CH$, $H_2C = CH_2$, $H_3C - CH_3$

sp sp^2 sp^3

"s character"

50% 33% 25%

قاعدة واقعة ضعيفة

$HC \equiv CH \rightleftharpoons HC \equiv C^{-} + H^{+}$

$H_2C = CH_2 \longrightarrow H_2C = CH^{-} + H^{+}$

$H_3C - CH_3 \longrightarrow H_3C - CH_3 + H^{+}$

4) Inductive effect

groups

donating
pushing
releasing

withdrawing

- يدفع كثافة الإلكترونية بسبب ناتجة عن الاختلاف في الكهروسالبية

- يدفع افتلاف في الكهروسالبية
تحتوي فقط على C_nH_{2n+1}

G → G ←

Ex: alkyl group الكيل العام C_nH_{2n+1}

CH_3 , C_2H_5 , C_3H_7

3rd lecture Introduction

Thursday 2-2-2020

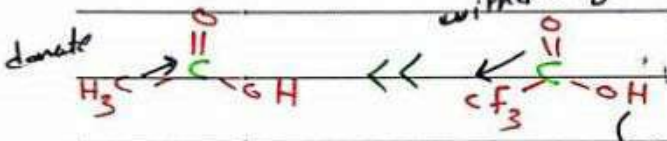
Note :

In general donate groups effect negativily on Acidity but withdrawing groups effect positivily on Acidity

Acidity دبكل عام المجموعات اللي donate تشكل سلبي على
Acidity : اما المجموعات اللي withdrawing تشكل ايجابي على

just in σ bond

* remember :
- donate just C, H
- withdrawing : F, ...
- يضعف قوة الـ OH = OH



يضعف قوة الـ OH بسبب قوة الالكترونيغاتيفية

$F-CH_2-OH$, $Br-CH_2-OH$, $Cl-CH_2-OH$

I II III

* ترتيبهم withdrawing تختلف بـ E.N

I > III , II

$F-CH_2-CH-SH$ $CH_3-\underset{\underset{F}{|}}{CH}-SH$

I II

كلما ك.د كلما ك.ب

كلما كان قريب من المجموعة اللي بعطية اللي ستفقد H كلما كان more Acidity

II > I

CH_3OH << CH_3SH (Acidity)

- كلما زاد الحجم يسهل فقدان H وبالتالي more Acidity.

CH_3OH >> CH_3SH (polarity) O–H, S–H

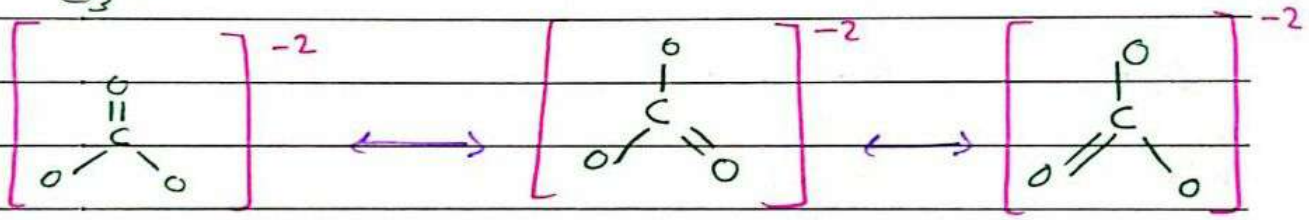
5- Resonance effect → in π bond. حيث

"Mesomeric" m effect

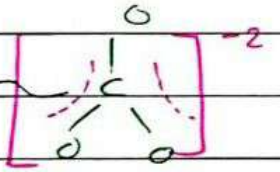
تأثير موضعي

Delocalization of e^- from place to another عن بعضها

CO_3^{-2}



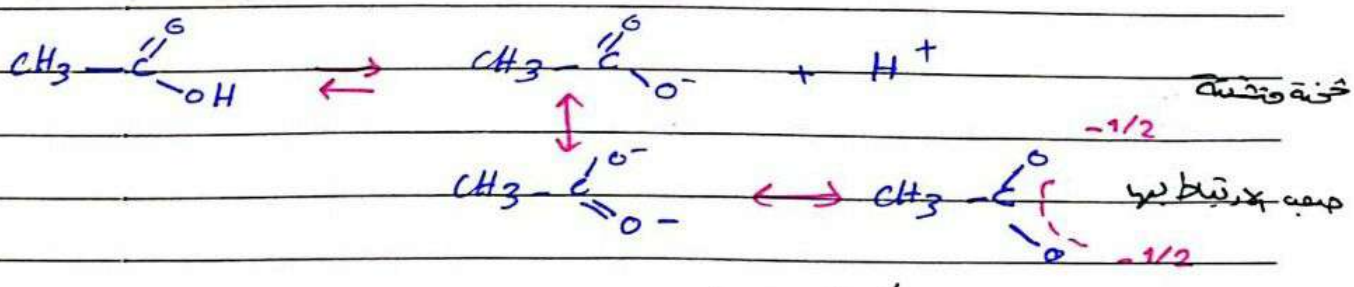
which mean that double bond isn't fixed.



* formela charge don't change befor and after resonance.

Which is more Acidity ?

$CH_3-C(=O)-OH$ or CH_3OH.



خلة مترافقة

صعب ارتباط بـ

conjugated weak

- عليه ارتباط H في مركب resonance صعب

$CH_3OH \longrightarrow CH_3O^- + H^+$

لأن حزمة ثابتة بيرد الارتباط بها

weak Acid — strong base.

6. Charge

- فقد H هو أيون متصل أصول بكثير من فقد H من أيون غير متصل

H_3O^+ — H_2O

Hydronume — water.

$H_3O^+ \longrightarrow H_2O + OH$

strong Acid — weak conjugated base

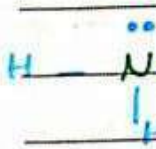
$H_2O \longrightarrow OH + H^+$

weak Acid — strong base

Basicity

- قدرتش أسرع في اعطاء زوج الالكترونات يكون more basicity

- مجموعة donate تؤثر إيجابياً في اعطاء الالكترونات.
- مجموعة withdrawing تؤثر سلبياً في اعطاء الالكترونات



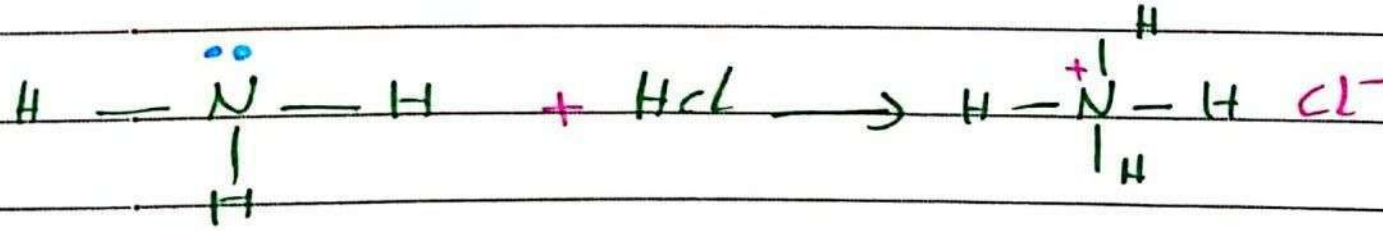
base ← lone pair كيوي

base + Acid → salt + water

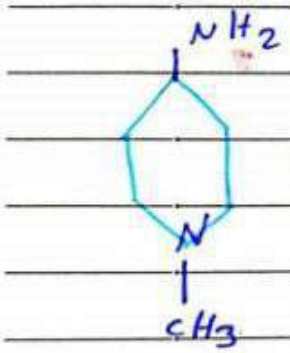
$NaOH + HCl \rightarrow NaCl + H_2O$

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

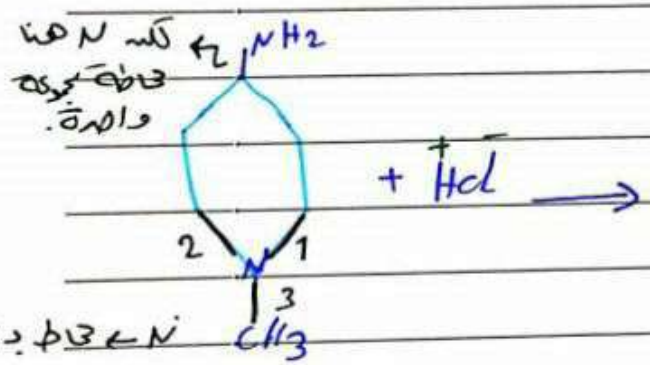
لي بتقلك كدا لانه قوي



If one mole of HCl is added to the following compound what is the expected product.

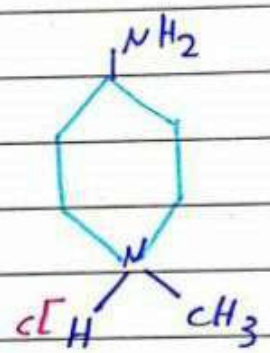


basicity زادت N زادت الإلكترونات كلما basicity تزداد donate



N عند كل ذرة N
واحدة.

3 عند N ذرة
مجموعات



Acidity.

دائماً التفاعل يتجه نحو الحمض الأضعف ← Pka أكبر

$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$

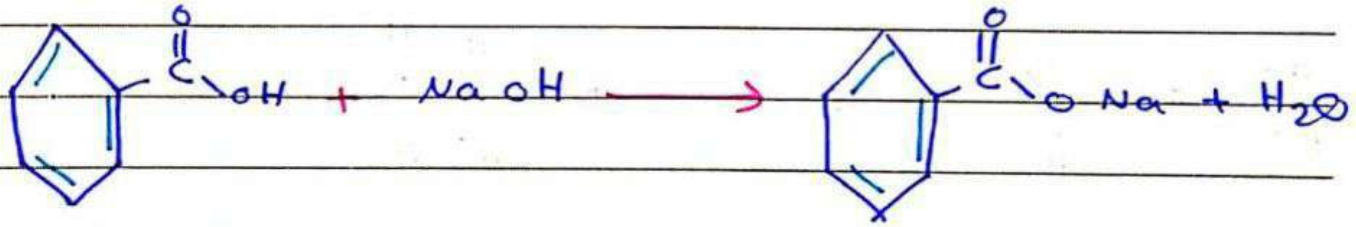
Pka 4.76 Pka 15.7

∴ occur.

$CH_3COO^- + HCN \longrightarrow CN^- + CH_3COOH$

Pka 9.31 Pka 4.76

∴ not occur.



Pka 4.19 Pka 15.7

∴ occur.

Chemical Reaction

In general : old bonds are broken and new bonds are formed

organic chemical Reaction

- what types of organic reaction?
- How the reaction occure " Mechanism "

- Types of organic chemical reaction :-

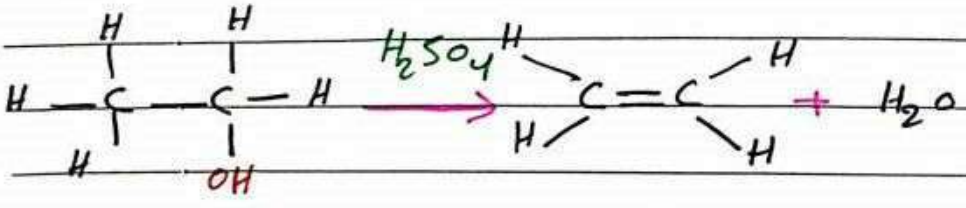
1- Addition reaction . 2 → 1 إضافة

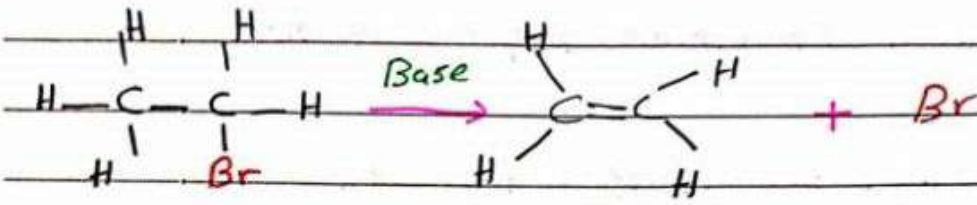
- Two reactant added togather to form new one product.
- occure in unsaturated compound ex: alkenes, alkynes

2- Elimination reaction : 1 → 2 حذف

- one reactant splits in to two product.

ex: alkyl halid , Alcoholes.

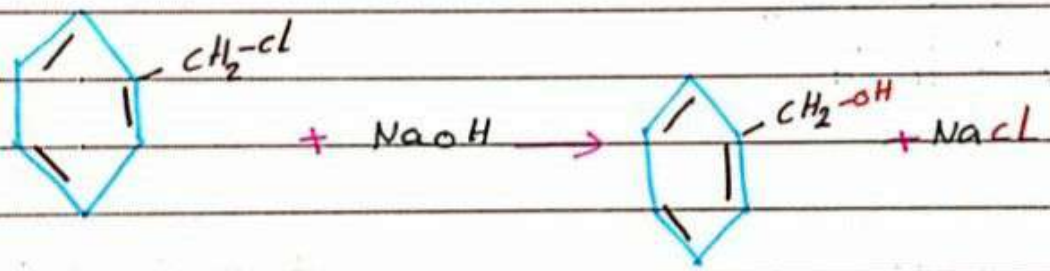




3. Substitution 2 → 2 تبادل

- Two reactant exchange parts to form product.

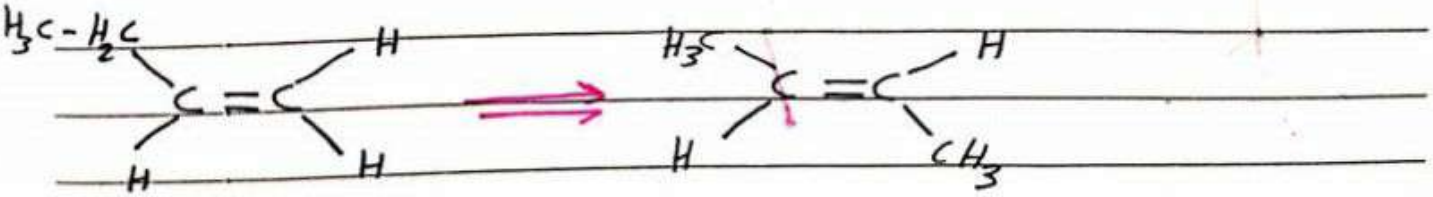
$AB + cD \longrightarrow AD + cB$



4 Rearrangement reaction: 1-1

- one reactant undergoes reorganized bond or atom to form isomeric product.

↳ The same in molecular formula but different in formula structure.



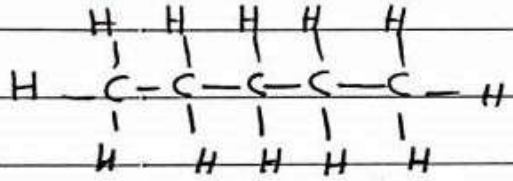
Chemical structure representation

1- Molecular formula = condensed formula

ex:

C_5H_{12}

2 dash formula



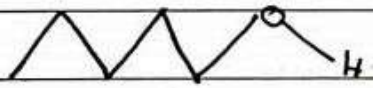
3- bond line formula

الأكثر شيوعاً، كل رأس يمثل C

لكنه يرفع إذا كان هناك ذرات غلاف H,C (hetro atom)

مثل (O S N)

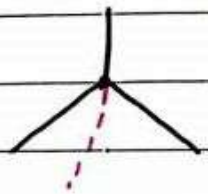
$C_5H_{12}O$



4- tetra hedral formula

مختص بالجزيئات العضوية

Stero chemistry



in the back

in the front

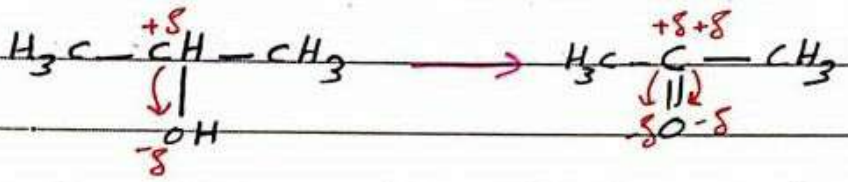
Redox in organic chemistry

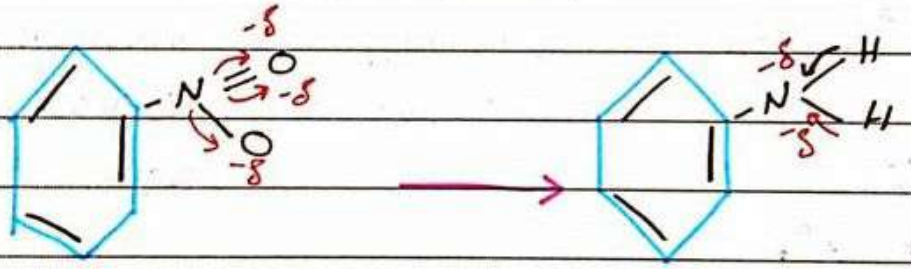
- oxidation: loss of electrons and higher oxidation state

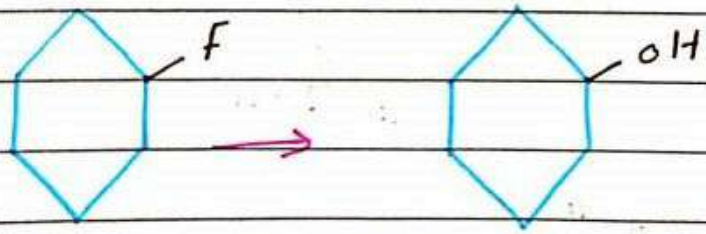
$$Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$$

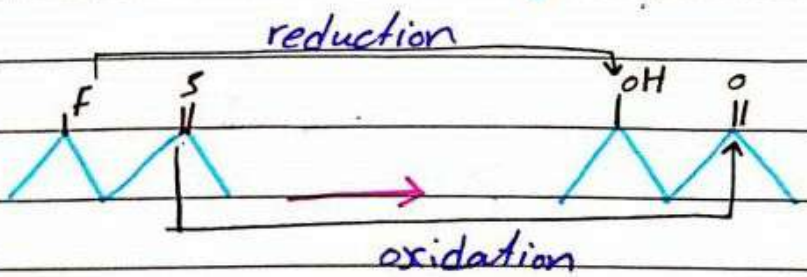
- Reduction: gain of electrons and lower oxidation state.

$$Fe^{+3} + e \longrightarrow Fe^{+2}$$









Disproportionation.

substance that has oxidation and reduction at the same time.

5 lecture

25.2.2020 tus.

Intermediates

$A + B \rightarrow [\ ] \rightarrow$ product

- intermediates or Transition state
- very fast and short life.

1- carbocation $-\overset{|}{\underset{|}{C^+}}-$ sp^2 planar trigonal

- Any factors minimize positive charge leads to increasing in the stability.

donate ← CH_3

$H_3C \rightarrow \overset{|}{C^+} \leftarrow CH_3$

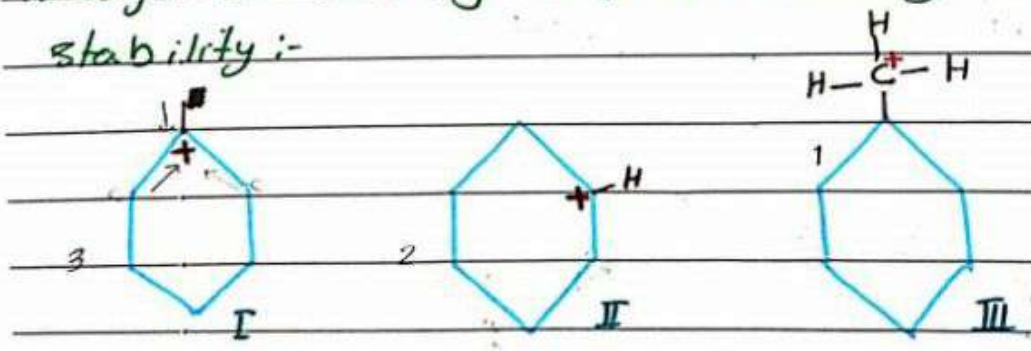
- كلما زادت مجموعات donate يزداد استقرار C^+ وذلك بالنسبة لبعضها لأن يقلل من شحنة الموجبة فتزداد بشكل

withdrawing ← NO_2

$Cl \leftarrow \overset{|}{C^+} \rightarrow F$

بعكس withdrawing وهي مجموعات عاملة فتقوم بسحب الالكترونات عنها وتزداد شحنة الموجبة فتقل بشكل.

Arrange the following compound according increasing in the stability :-



$> \quad >$

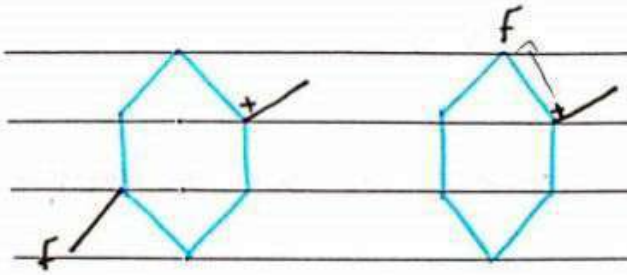
∴ F عبارة عن withdrawing تقوم

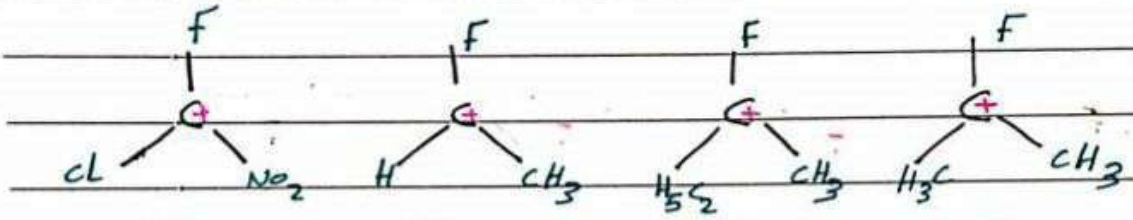
بعملية سحب لـ e وبالتالي كلما اقتربت من C^+

كلما كان قوة السحب أكبر وبالتالي تزداد

استقرار الكاتيون في حين لو ابتعدت تقل

قوة السحب فيقل سحبها للالكترونات.





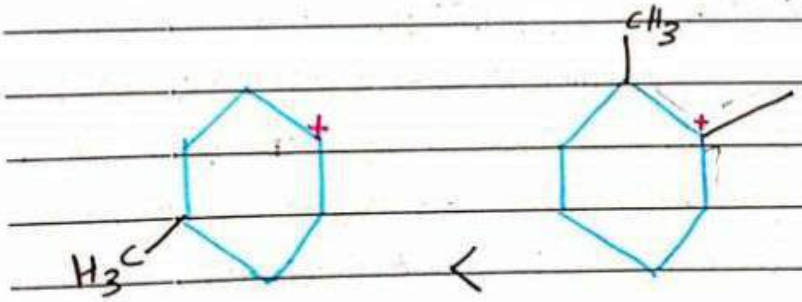
I II III IV

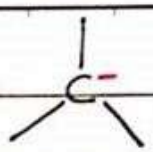
III > IV > II > I

المركب الأول عمليا ليس بالتالي يكون

أقل مركب المركب الثاني تحتوي على مجموعة ألكيل واحدة

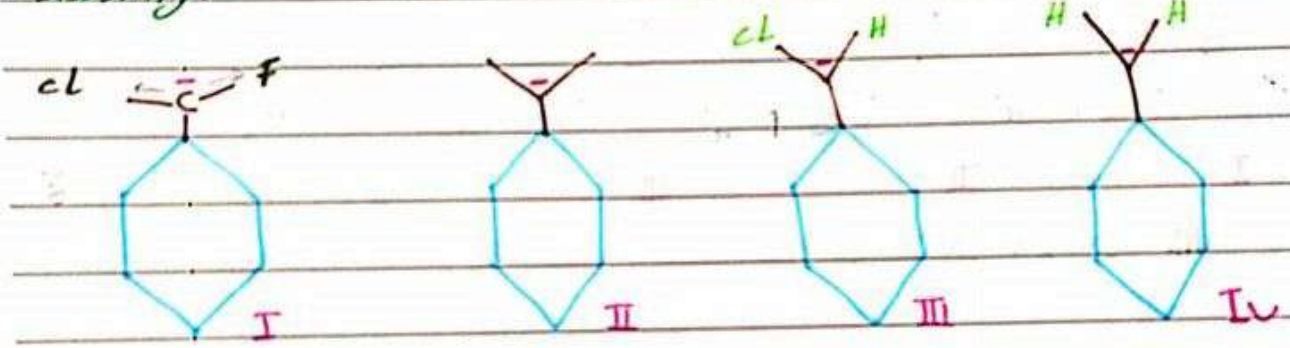
في حين باقي هم فجميعهم أما ثلاثة وقد ازدادت فيهم ذرات الكربون وبالتالي يكون استقرارهم



2 carboanion.  sp^3 tetrahedra

- Any factors minimize negative charge leads to increasing in the stability.

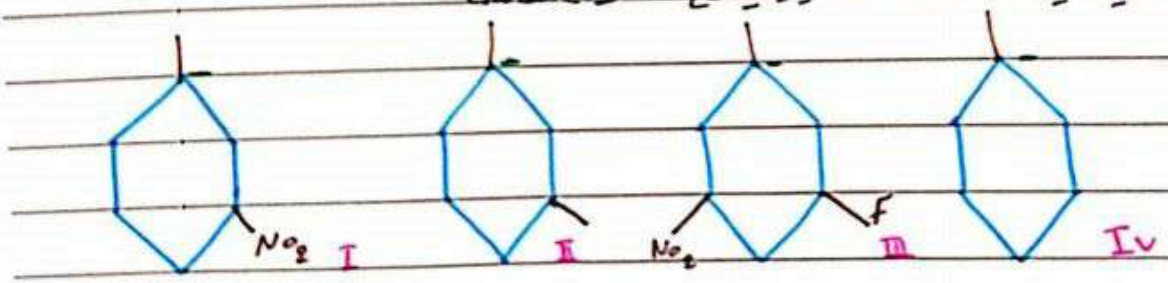
Arrange the following compound according increasing in the stability.



* الهدف هو تقليل الشحنة السالبة وذلك عن طريق e.w.d التي تقوم بسحب الالكترونات بالتالي زيادة + فتقل من stability وتزيد

- في المركب I يوجد 2 مجموعة e.w.d لذلك هو الأقل ، ثم III يليه ثم II يحتوي على مجموعة e.w.d واحدة لكن مركب Iv يحتوي على donate ، فالمركب الذي يحتوي على donate أقل من stability لأن donate يعمل على زيادة الشحنة السالبة

واحدة في حين أن II يحتوي على donate.3

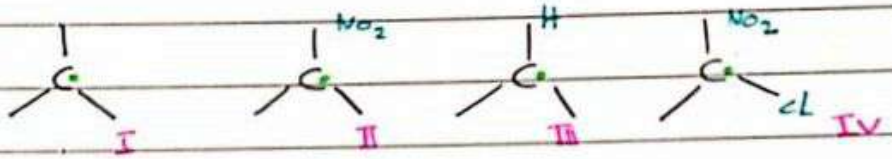


III > I > Iv > II

3. Free Radical

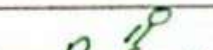
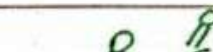
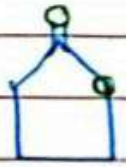
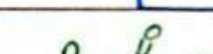
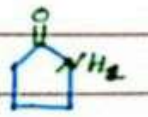
sp^2 trigonal planar يكمل الالكترون فرد

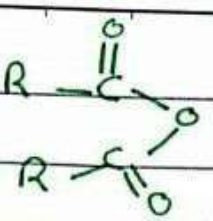
- كل ما ينطبق على carbocations ينطبق على Free radical



I > III > II > IV

Functional groups.

1. alkane 
2. alkene 
3. alkyne 
4. alkyl halide R–X
5. Aryl halide Ar–X
6. Alcohole R–OH
7. Thiole R–SH
8. ether R–O–R
9. thioether R–S–R
10. Aldehyde 
11. Ketone 
12. Carboxylic Acid 
13. ester 
14. lactone  cyclice of ester
15. Amide 
16. lactam  cyclice of Amide

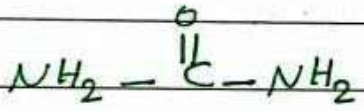
17- Acidanydride 

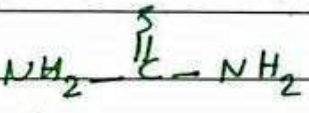
18- Amin $R-NH_2$

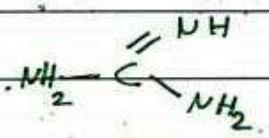
19- Azide $R-N_3$

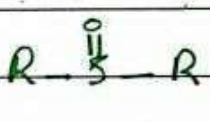
20- Nitril RCN

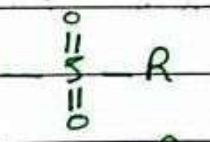
21- diazonium salt $Ar-N^{+}\equiv N\ x^{-}$

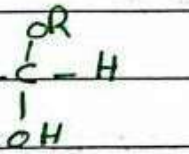
22- urea 

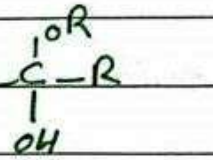
23- Thiourea 

24- guanidine 

25- sulfoxide 

26- sulfone 

27- hemi acetal 

28- hemi ketal 

29. acetal $R-C(OR)(OR)-H$

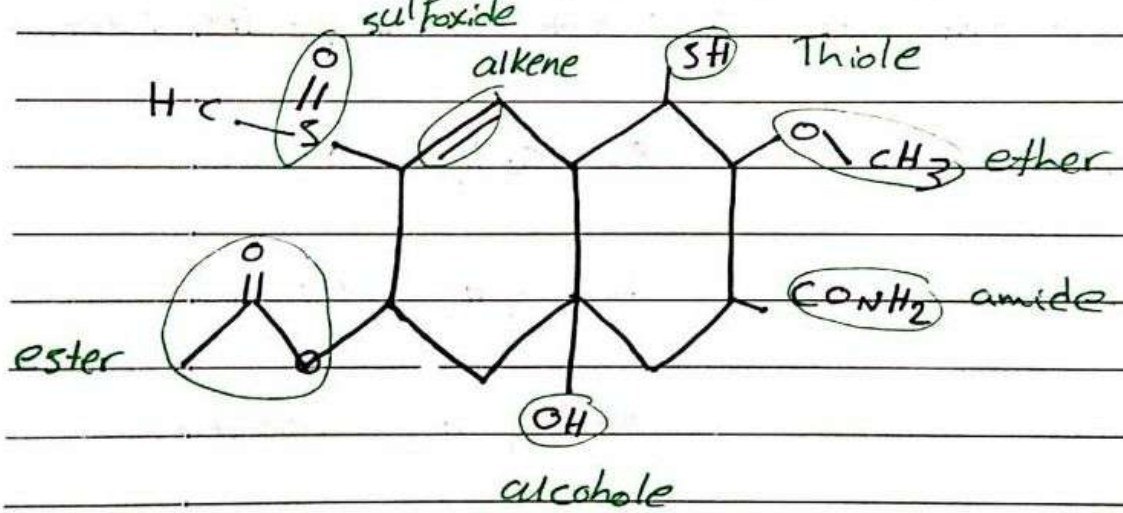
30. ketal $R-C(OR)(OR)-R$

31. Nitro NO_2

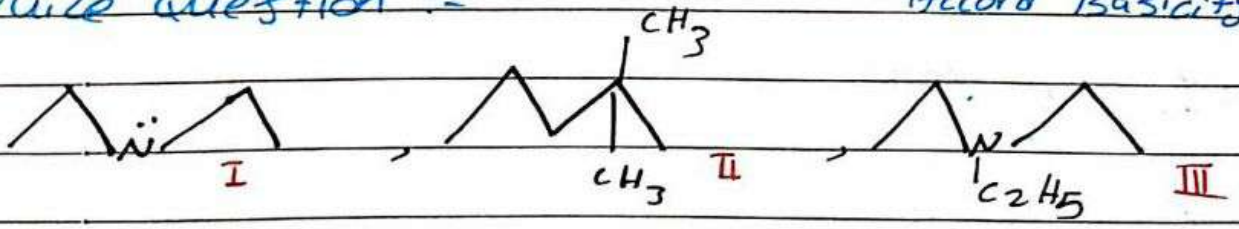
32. Q20 $R-N=N-R$

33. Hydrazine NH_2-NH_2

Name each of the functional group in the arbitrary structure



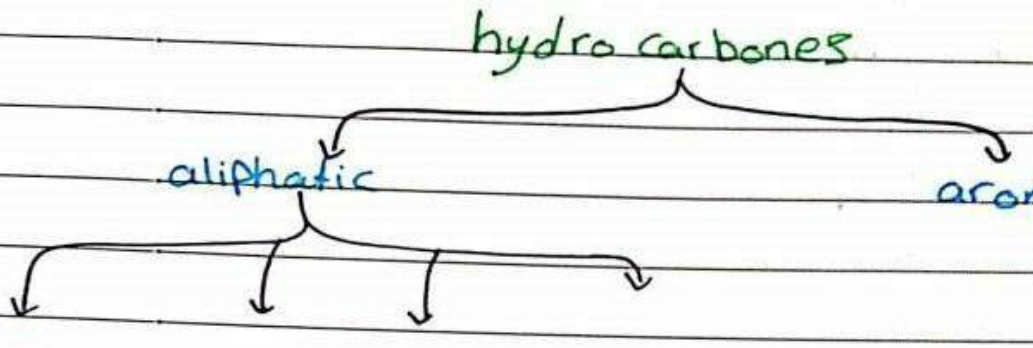
Quize question :- Accord Basicity.



3 > 1 > 4 > 2

Chapter 2, 6 lecture

27.2.2020
Thursday



alkanes alkenes alkynes cycloalkane
"Alicyclic"

Alkanes = parffines

- Saturated Hydrocarbone compound containe only C, H
- inert compound : Because it's contain just C, H which there's no different in E.N between C, H so it's inert.

1- CH_4 methane

2 C_2H_6 ethane

3 C_3H_8 Propane

4 C_4H_{10} butane

5 C_5H_{12} pentane

6 C_6H_{14} hexane

7 C_7H_{16} heptane

8- C_8H_{18} octane

9- C_9H_{20} nonane

10 $C_{10}H_{22}$ decane

$C_4H_{10} \rightarrow C_4H_9$ butan → butayl

$C_8H_{18} \rightarrow C_8H_{17}$ octane → octyl

Properites of alkanes

1- Physical state

$C_1 \rightarrow C_4$ gase

$C_5 \rightarrow C$ liquid

Tell why ??

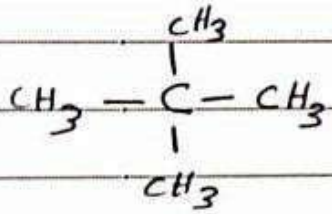
* propane is gas while hexane is liquid. ?

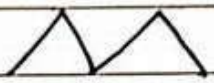
2 non. polar compound.

C, H No different in E.N.

3- boiling Point B.P.

M.W ↑ ↑ B.P





- كلما كانت قوة التماسك أقل كلما كانت احتياجها لطاقة لكي ترابطة أقل.

branching 9.5°

chane 36°

لكلما Branching يضعف يثبت ترابطة وبالتالي تقل في درجة الغليان لكلما chane تكون قوة التماسك أقل

Namenclature of alkanes:

- Common Name
- IUPAC Name (International union of pure and Applied chemistry)

prefix
- what is substituent? مستبدلات

parent
How many C?

suffix
what is functional group??

• Rules of Nomenclature :-

1- Find the longest cheine أطول سلسلة

2- Number near the branching نرقم بحيث المتبدل يأخذ أقل رقم ممكن

3- Name the substituent with their number نسمي المتبدل بأرقامها

4 Arrange the substituent alphabitically.
إذا لم يُذكر الرقم فهي تعتبر 1

Substituent.

halogen = halo NO_2 : Nitro (e,y) المتبدلات تنتهي بـ

F → fluoro

Cl → Chloro NH_2 : Amino.

Br → Bromo

I → Iodo.

- عند اختيار أطول سلسلة لا نرجع إلى ورائنا ويشترط أن تكون chein متكونة على شكل

2: di : 8: octa

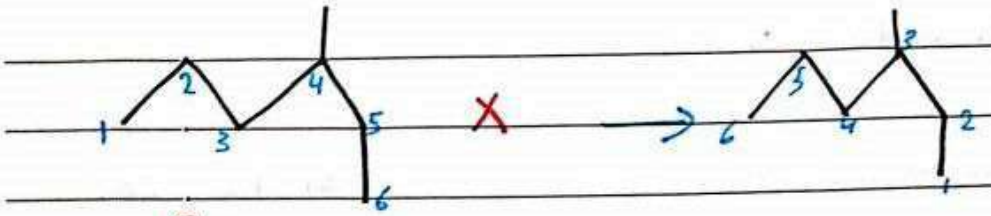
3: tri 9: nona

4: tetra 10: deca

5: penta

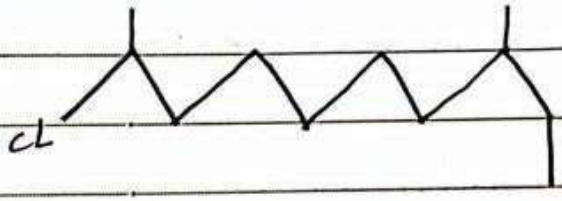
6: hexa

7: hepta.



3- methyl hexane.

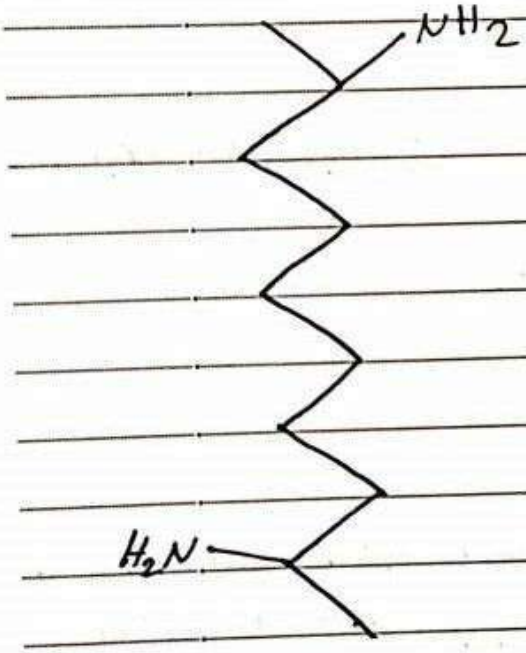
False



2- chloro -8- methyl decane.

3+9 = 12 ✗

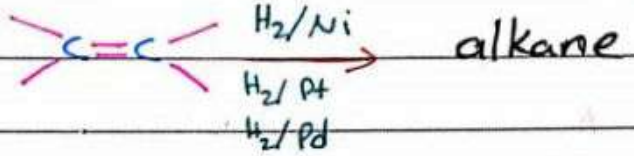
2+8 = 10 ✓

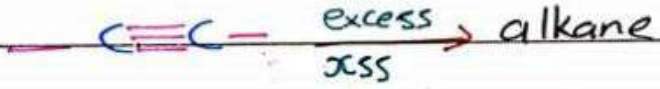


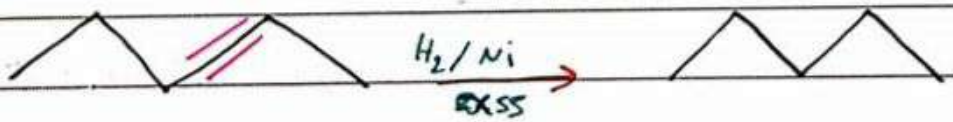
2,9 diamino decane.

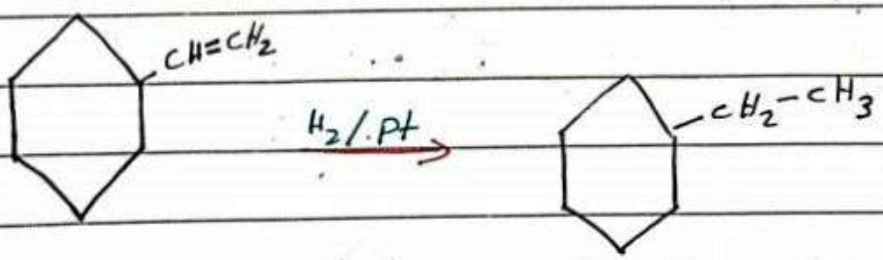
Preparation of alkanes :-

1- Hydrogenation of unsaturated compound. (alkenes, alkynes)



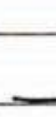




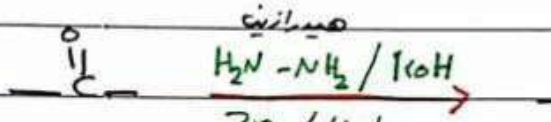


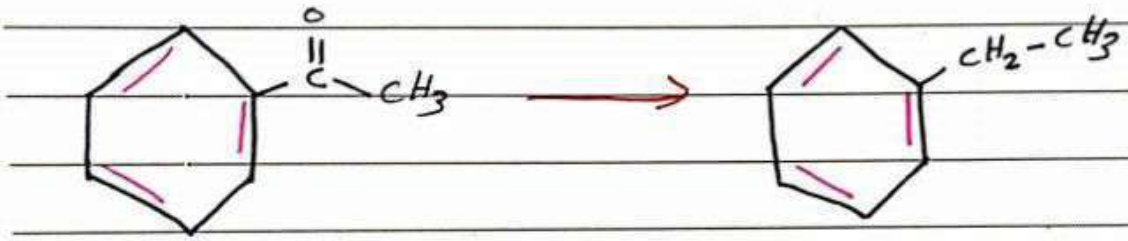
2 Reduction of carbonyl group [only aldehyde and ketones]

* يتم بالوسط الحمضي والقاعدي.

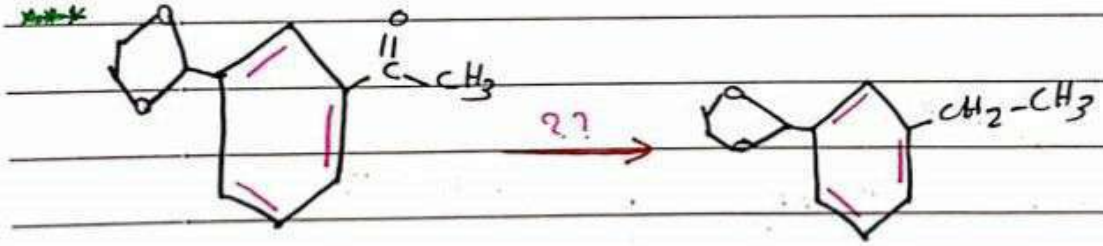


carbonyl group





* تحتفظ بعدد ذرات الكربون.



* ?? ⇒ NH_2-NH_2 / KOH Because  stay the same Because it's sensitive for Acidic media.

3/1.

3. Hydrolysis of Grignard Reaction:-

$R-MgX$ — alkyl — halogen

$Ar-MgX$ — Aromatic

$R-X \xrightarrow[\text{dry ether}]{Mg} R-Mg-X$

alkyl halid

$Ar-X \xrightarrow[\text{dry ether}]{Mg} Ar-Mg-X$

aryl halid

$\overset{\delta+}{R}-\overset{-\delta}{X} \Rightarrow \overset{-\delta}{R}-\overset{+\delta}{Mg}X$

Mg يكسب عنه كهرب

very basic أصبح مركب R أذ δ- وهذا يعني أنه مركب أصبح

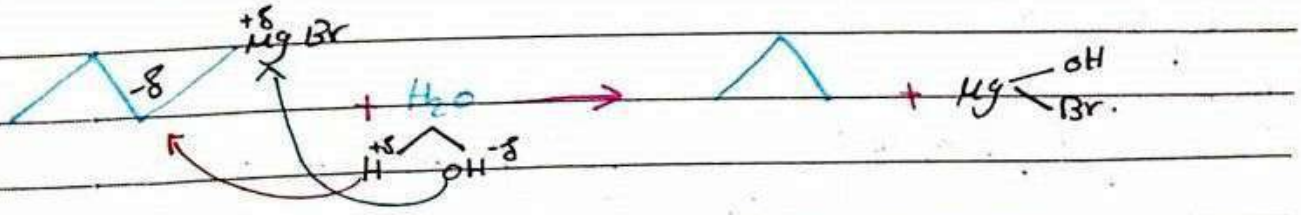
"neuclophillic"

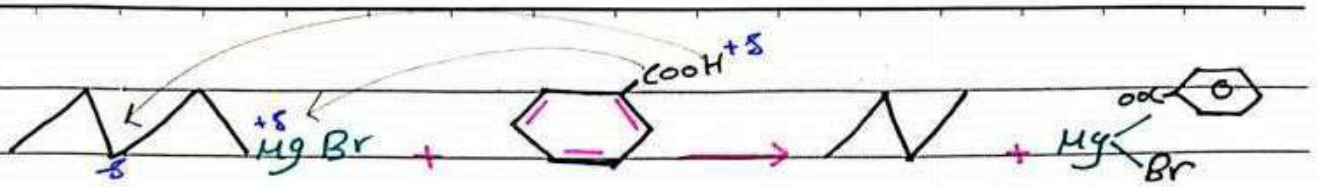
$\overset{-\delta}{R}-\overset{+\delta}{Mg}X + \text{weak Acid} \longrightarrow \text{alkane}$

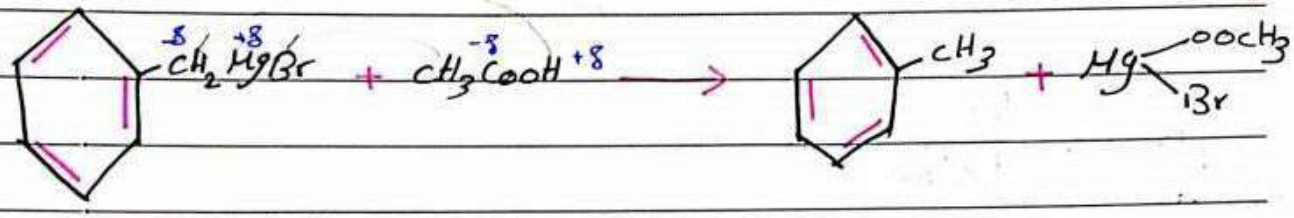
عند كربات الكربون كاهي.

very basic

weak Acid.







Note :

If one of this metal (Mg, Li, Na, K) inter between R, X

R–MgX ⇒ Grignard reaction ⇒ organometalic compound.

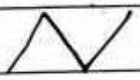
4. Wurtz Reaction :- symmetric doublication تضاعف متماثل

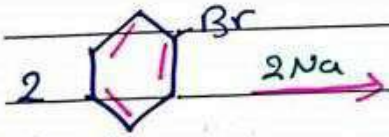
$$2\ R\text{–}X \xrightarrow{2Na} R\text{–}R$$

alkylhalide

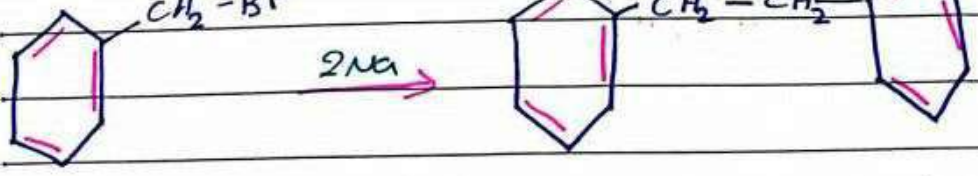
$$2\ Ar\text{–}X \xrightarrow{2Na} NR$$ no reaction.

Ex:

$$2\ CH_3\text{–}CH_2\text{–}Br \xrightarrow{2Na}$$ 



Aromatic cycle.

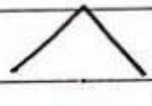


in this reaction there is CH_2 between the cycle and Br

so the perfect answer is to doublicate.

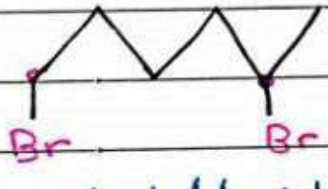
$2\ CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{2Na}$ NR

in this NR theres No halide ✗ hahaha

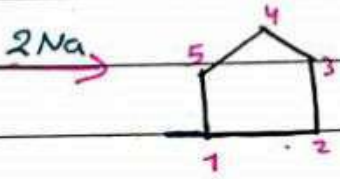


→ alkyl halide.

• intra molecular cyclization → process of cyclization occure just in dihalide

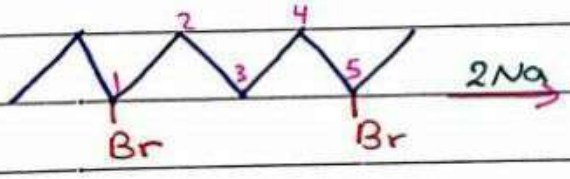


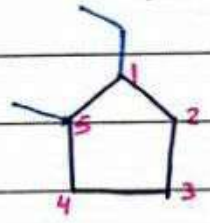
alkyl dihalide

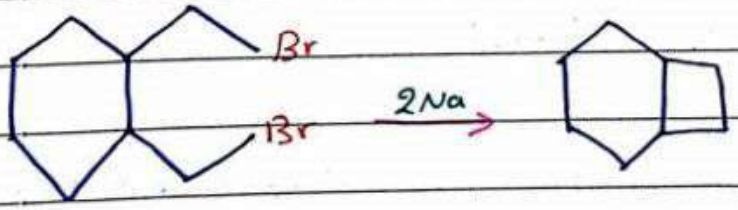


+ 2 Na Br

في حالة alkyl dihalide ← نفس عدد ذرات الهالوجينات ← ثم نقوم بعمل حلقة دفعة بعشوائي عشان شكلوا والترقيم لكن يجب دفع الرقم وتوفير التفوق.







كذلك يحافظ بنفس ذرات الهالوجين وتعمل حلقة بالوسط

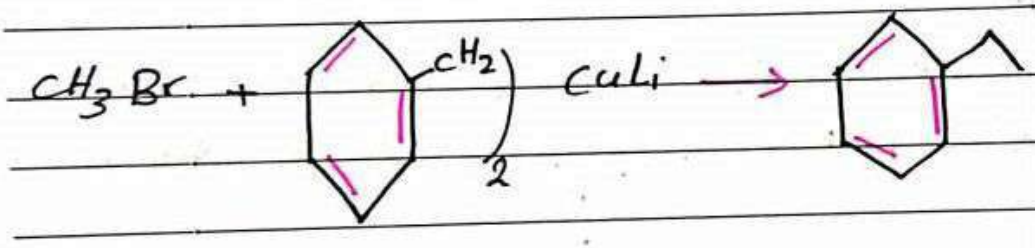
5- Corye house reaction :- Asymmtrical carbon to get
"To produce longer alkane"

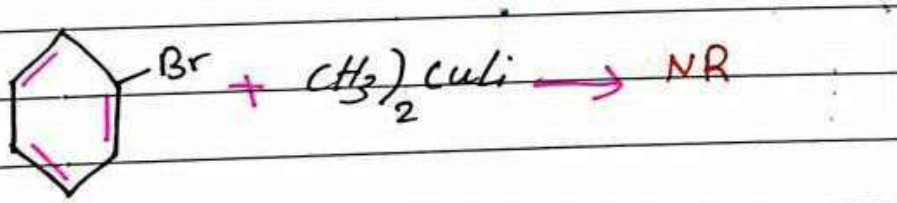
$$R-X + R'_2\,CuLi \longrightarrow R-R'$$

$$CH_3-Br + (CH_3CH_2)_2\,CuLi \longrightarrow CH_3-CH_2CH_3 \text{ or } \text{cyclopropane}$$

or $CH_3-CH_2-CH_3$

$$Ar-X + R_2\,CuLi \longrightarrow NR$$





6- Decarboxylation of carboxylic Acid :-

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[(NaOH+CaO)]{\text{"Soda-lime"}} R-H$$

"alkan"

$-CO_2$

R → Alkyl + H → alkan

7) Reduction of alkylhalide

$$R-X \xrightarrow{Zn/HCl} R-H$$

alkane.

• Reaction of alkane :- * :: Alkanes are inert compound so its reactions are rare.

1) halogenation

$R-H \xrightarrow[Light]{X_2} R-X + H$ "Free radical substituation"

- WARNING
- without Light ⇒ NR.
- exisist of H to make substituation

F_2 very reactive

Cl_2

Br_2 > the most uses

I_2 → inert

• Mecanism of halogination :-

1) Initiation بدء

$X_2 \xrightarrow{Light} X^\cdot + X^\cdot$ Transfair the halogen to free radical.

2) propagation تفرع

$X^\cdot + R-H \longrightarrow R^\cdot + HX$ * the X Bonded ب H because of it's small size

$R^\cdot + X-X \longrightarrow R-X + X^\cdot$

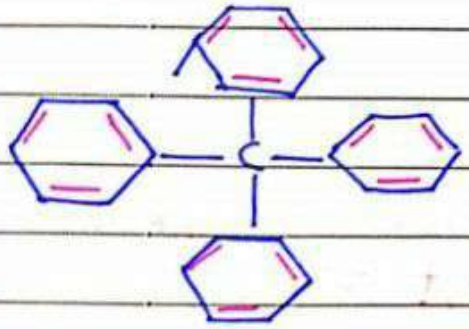
3) Termination.

$X^\cdot + X^\cdot \longrightarrow X_2$

$R^\cdot + R^\cdot \longrightarrow R_2$ or $R-R$

$X^\cdot + R^\cdot \longrightarrow R-X$

$CH_3-CH_3 \xrightarrow[Light]{Br_2} CH_3-CH_2-Br + HBr$



$\xrightarrow[Light]{Br_2}$ NR There's No H

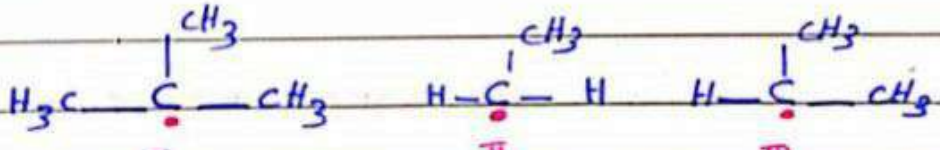
$CH_3-CH_2-CH_2^{\bullet}$

derivate $\rightarrow$ ✓ $CH_3-\overset{\bullet}{C}H-CH_3$ $\leftarrow$ The most stable *

$^{\bullet}CH_2-CH_2-CH_3$

$CH_3-CH_2-CH_3 \xrightarrow[Light]{Cl_2} CH_3-CH_2-CH_2-Cl + HCl$ ✗

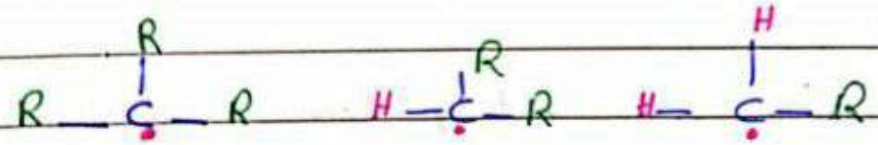
* Remaber carbocation and freeradical.



"stability".

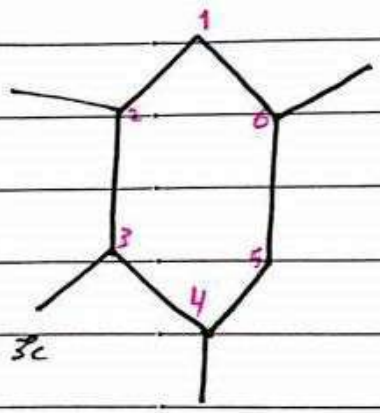
I, II, III

I > III > II

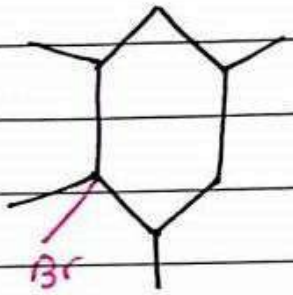


3°c 2°c 1°c

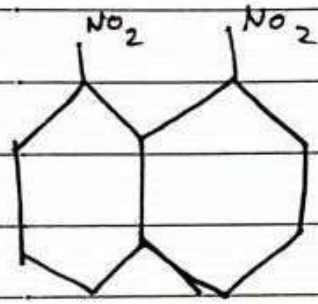
ter sec Primary



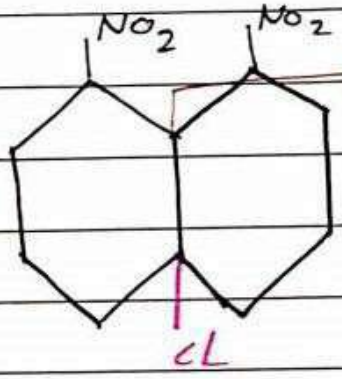
Br_2 / Light →



* As he said which c is more stability.



Cl_2 / Light →



we don't but cl because it's near to withdrawing group.

conversion : تحويل

A → B

$CH_3-CH_2-CH_2-Br$ To 

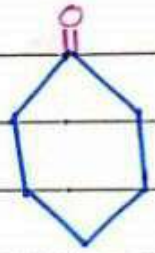
$CH_3-CH_2-CH_2MgBr \leftarrow CH_3-CH_2-CH_2-Br$

↓

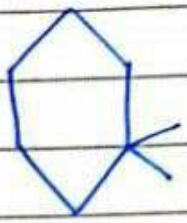
$CH_3-CH_2-CH_3$

↓ Br_2 / light

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ = 



To

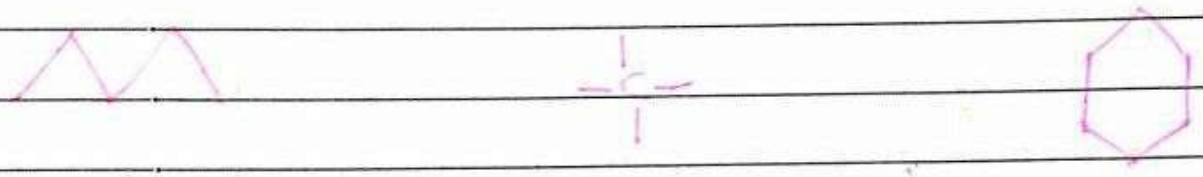


Cyclo alkanes 9th lec.

5.3.2020, Thursday

Alkanes

chaine — branch — cyclic



- when the carbon atom arrange to form cycle is called cyclo alkane

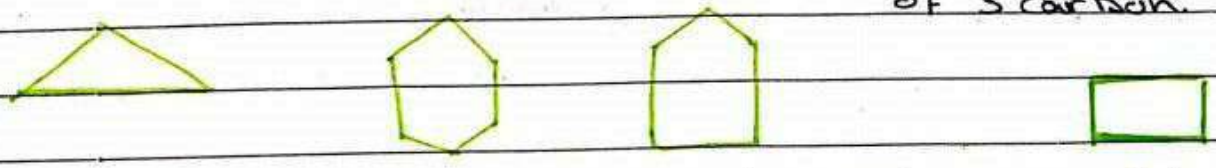
- when alkane decrease {H atome} even it's chaine or branc or cyclic it become alkyle.

cyclo alkane

unsubstituted — substituted

Note :

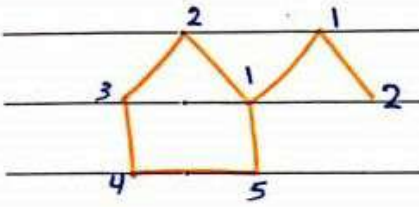
- Nomenclature of cyclo alkane :- The less cycle contain of 3 carbon.



cyclopropane — cyclohexan — cyclopentane — cyclobutane

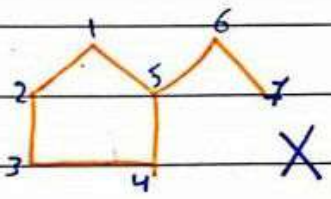
- un substitued cyclo alkane

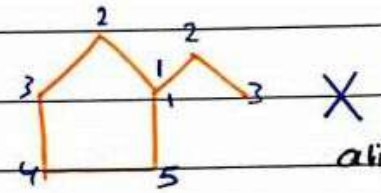
• substituted cyclo alkane :- إذا عدد ذرات ال أكبر هو الأساس والباقي نعتبره chain كي أنه chain ترقيمها يختلف كلياً عن cyclic



✓ 1 (ethyl) cyclo pentane

• المستبدل يأخذ أقل رقم ممكن

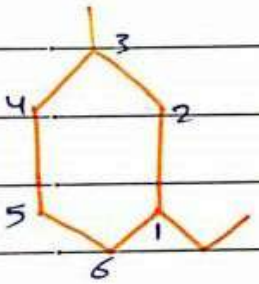
But:  X

 X

1+6 = 7 X

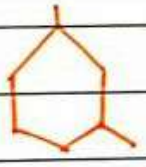
1+3 = 4 ✓

* اذا كان عدد ذرات aliphatic أكبر من عدد ذرات الأروماتيك يكون الأساس هو الأساس والكلمة تكون على شكل مستبدل.

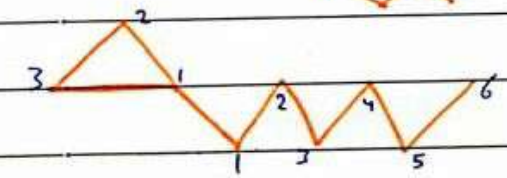


1_ethyl_3-methyl cyclo hexane.

* أما إذا كان عدد ذرات الكلمة أكبر



فتكون الكلمة هي الأساس 1,3 dimethyl cyclohexan



cyclopropyl hexane.

- اذا كانوا نفس العدد الأولوية للكلمة cyclic

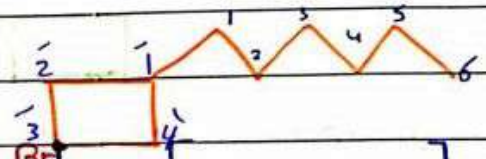
والـ chain تعتبر مستبدل.

butyl cyclo butan

- يجب أن يختلط ترقيم aliphatic بـ cyclic

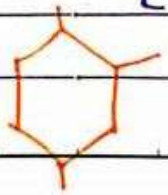
- عندما يكون لدينا poly substituted أو bisubstituted

- يجب أنه يكون مجموع الـ substituents أقل ما يمكن.



1 [3-bromo-cyclo butyl] -hexan

مستبدل بقلب مستبدل

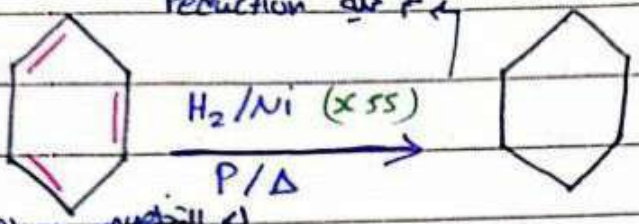


1,2,4 tri methyl cyclohexan.

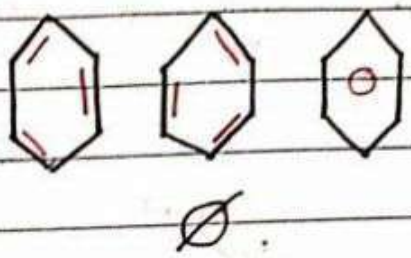
Preparation of cycloalkanes :-

Benzene

1- hydrogenation of benzene.



لا التخصيص ← بواسطة الضغط وإزالة

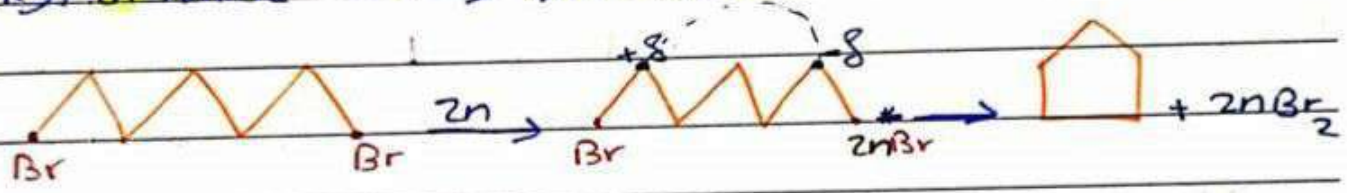


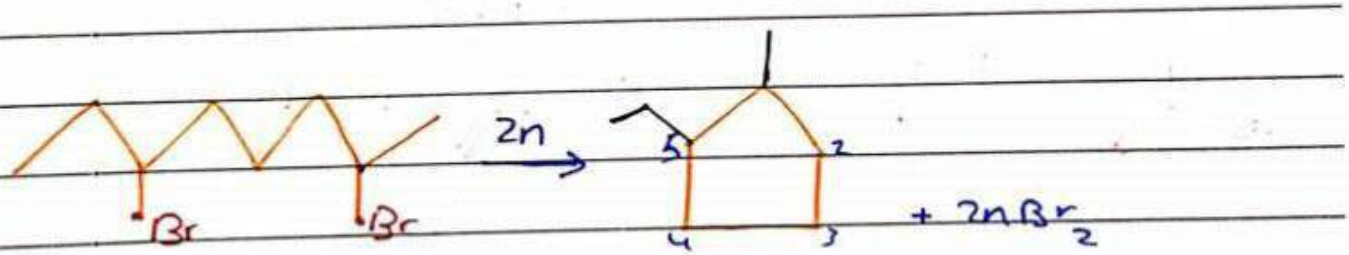
2- Freund Reaction :- "Intramolecular cyclization"

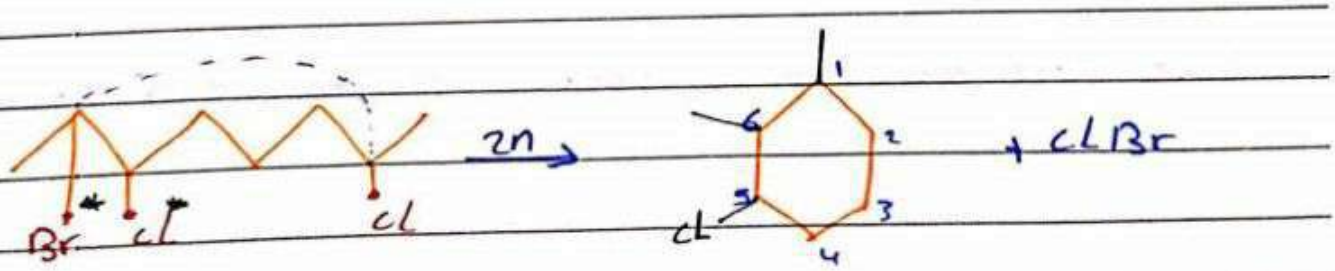
* C أصبح كهروسالبيته 2n لذلك 2n أكبر C غنية δ-

alkyl di halide $\xrightarrow{2n}$ cycloalkane.

δ+ 2nBr







- الأسهل بالفقد هو Br وليس Cl لأنه حجم Br أكبر من حجم Cl لذلك تتكون بين Cl، Br وليس بين Cl، Cl كذلك بين Cl^*، Br^* لاحتمال أنه يحدث cyclization لأنه عبارة عن تشبع كربون، الحلقة يلزمها 3 ذرات كربون على الأقل

***

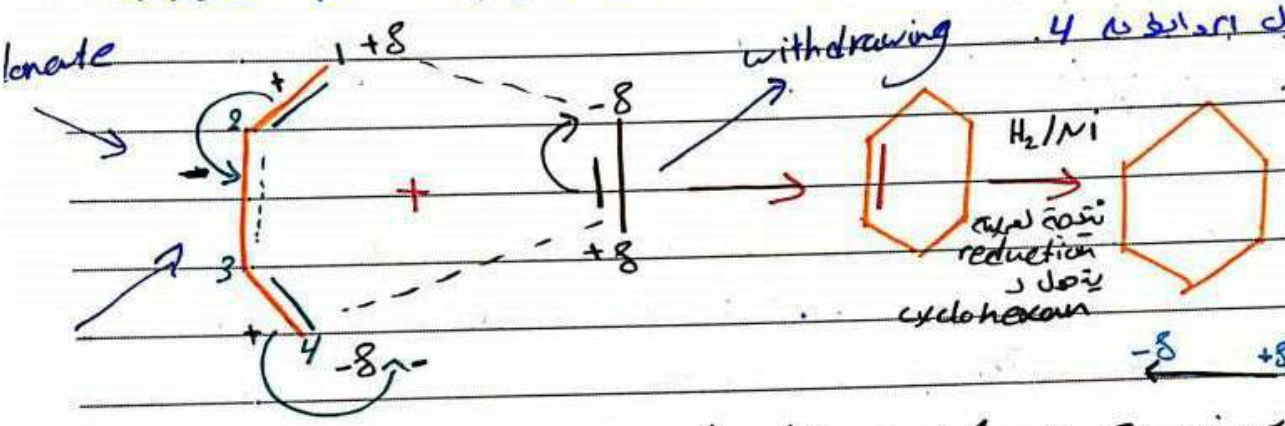
3. Diels _Alder Reaction :- Just in cyclohexane

1,3 dienes + alkenes → cyclohexene $\xrightarrow{red}$ cyclohexane.

= ديينات .

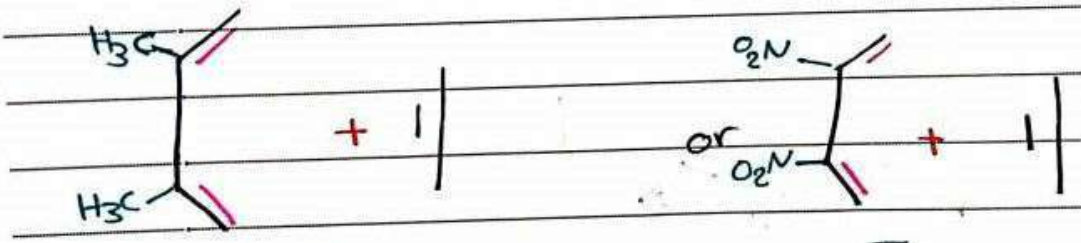
نتيجة الكواشة تتحلل الرابطة ما 1 إلى 2 وبالتالي يصير عندنا 3 ← 5 روابط.

لذا تتحلل الرابطة 4.



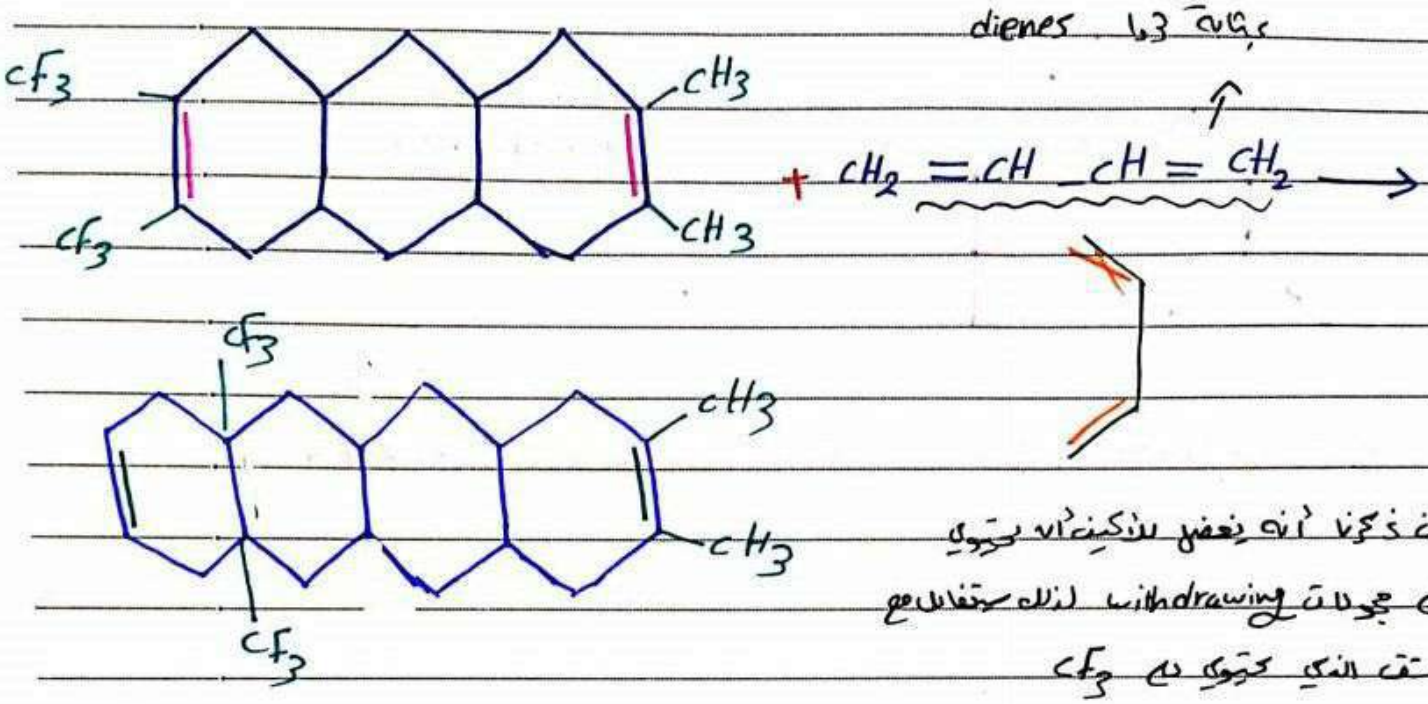
1,3 dienes

donate ← 3,1 لذا يجب أن يكون عندنا withdrawing. في المجموعة 1

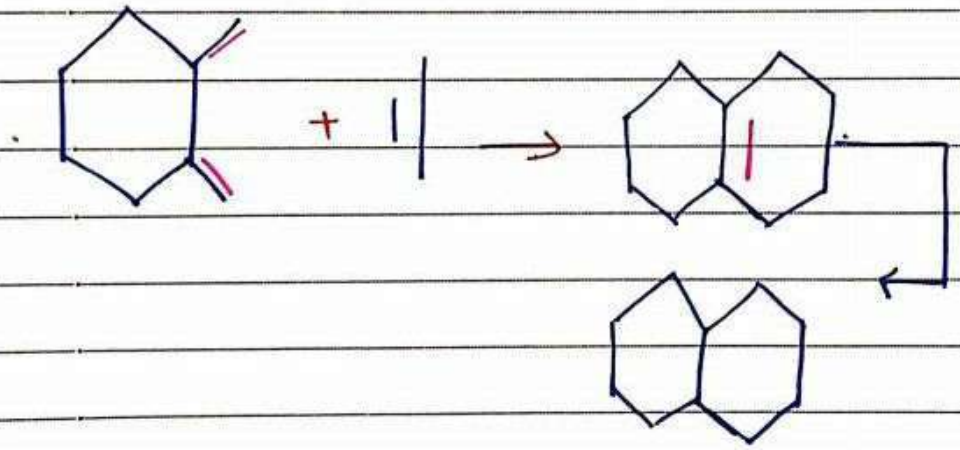


I II

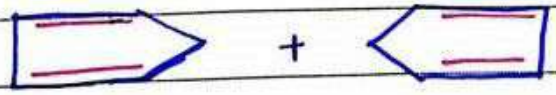
I is more easy than II because the present of donate group CH_3.



وكنت ذكرنا أنه يفضل للأكينات أن يحتوي
على مجموعات withdrawing لذلك سيتفاعل مع
الـ C=C الذي يحتوي على CF_3

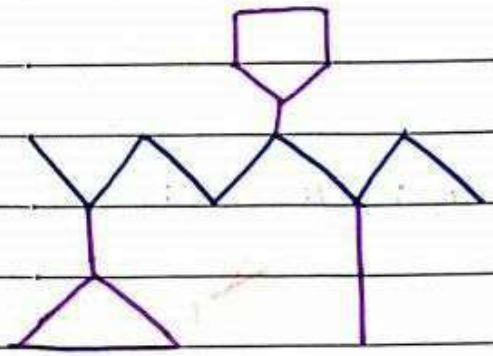


Think :-



cycloalkanes 8th lec.

5/4/2020. Sunday
1st electronic lec.



2+5+6 = 13 ✓
3+4+7 = 14 ✗

2-cyclopropyl-5-cyclopentyl-6-methyl-octane

Alkenes

10th lec.

6/4/2020

2nd electronic lect.

Alkenes:-

unsaturated hydrocarbon contains double bond.

C_nH_{2n}

C=C (π, σ) → so alkenes is more reactive than alkan due to the exist of π bond because it is more easy in broken the bond

- Nomenclature of alkenes:-

1 search for the longest chain in the compound

2 doublebond = has to take the less possible number in the longest chain.

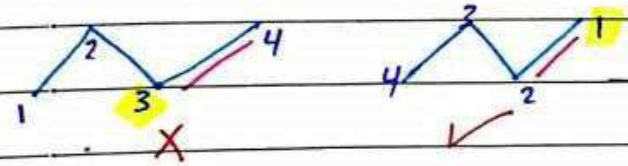
Note: If the compound contain more than one doublebond

2 doublebond → dienes

3 double bond → trienes

4 double bond → tetraenes

ex:

1) 

→ butene

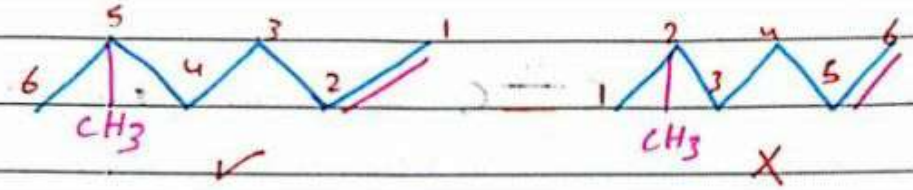
2)  → 2-pentene or pent-2-ene

3)  → 1,3 hexdienes or hex 1,3 dienes.

1+3=4 ✓

3+5=8 ✗

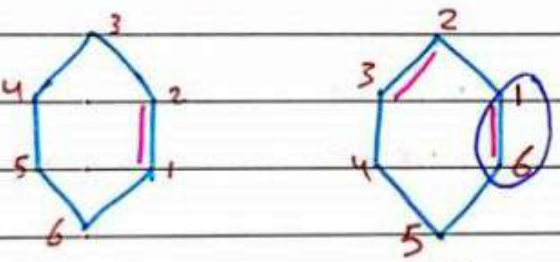
• If the compound contain both the double bond and substituted the priority for the double bond.



✓ X

5-methyl hexene.

• Nomenclature of cycloalkenes :-

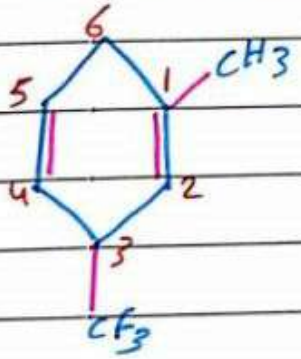


cyclohexene X 1,3 cyclohexdienes or cyclo hex 1,3 dienes.

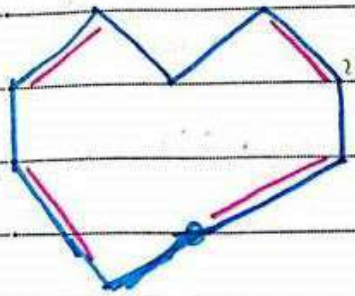
لا نستخدم رقم 1 في الحلقة

* Name the following compound :-

1)

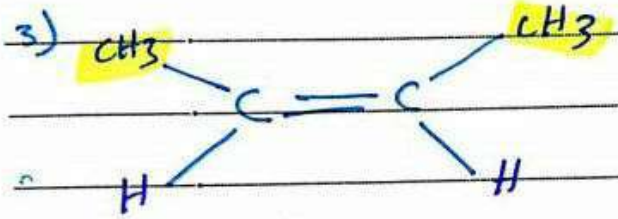


1-methyl-3(trifluoromethyl) 1,4 cyclohexdienes

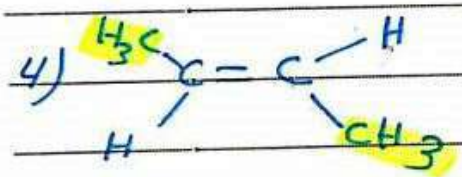
2) 

1+3+5+7 = 16

1, 3, 5, 7 non tetraenes.

3) 

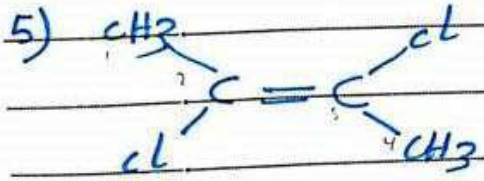
Cis but-2-ene or 2-butene.

4) 

Trans but-2-ene or 2-butene

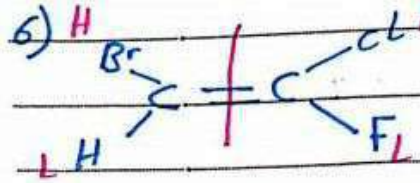
Note :- Cis : when the substituteds are the same

Trans : when the substituteds are different.

5) 

Trans 2,3 dichloro but-2-ene.

في هذه الحالة نقسم الـ C إلى قسمين ونقارن المجموعات

6) 

High الأعلى تأخذ Atomic number عدد ذري

والأقل تأخذ Low إذا كانوا H H

مقابل بعضه تأخذ Z وإذا كانوا مختلفين تأخذ E

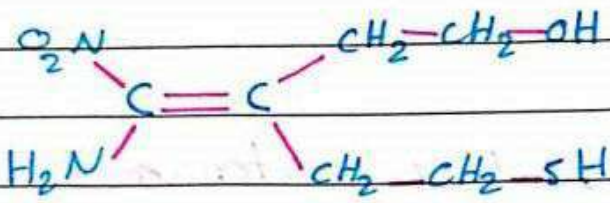
Z

complet of alkenes. 11th lec.

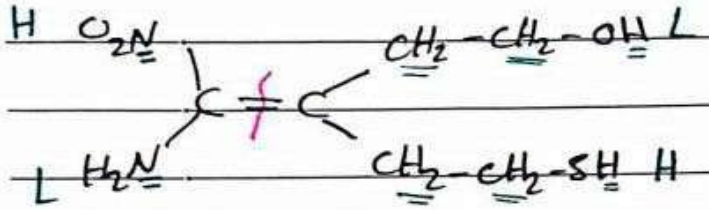
7/4/2020 Tuesday

3rd electronic lecture

7)

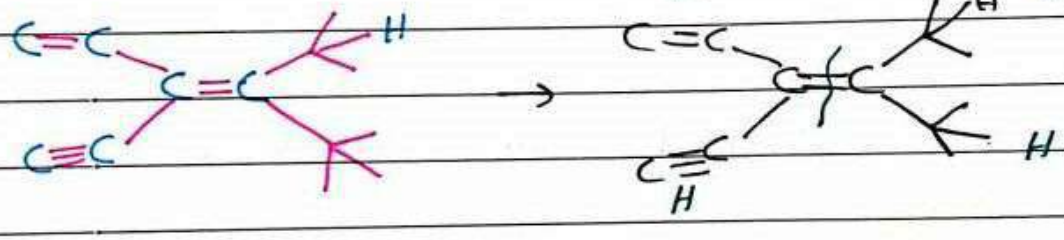


في حال تشابه الذرات ننتقل إلى ذرات أخرى.



E

8)

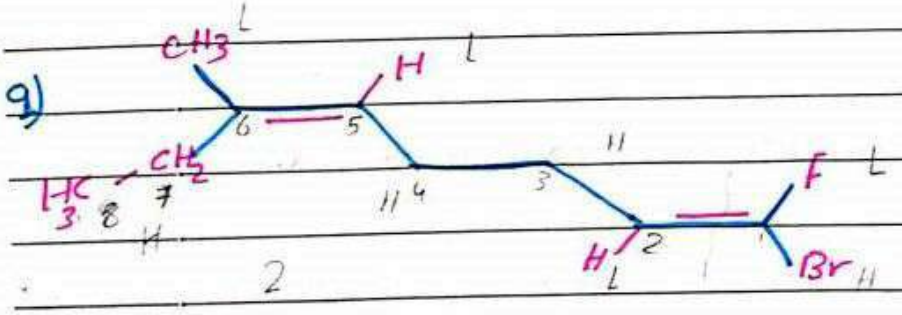


* C=C : L

Z

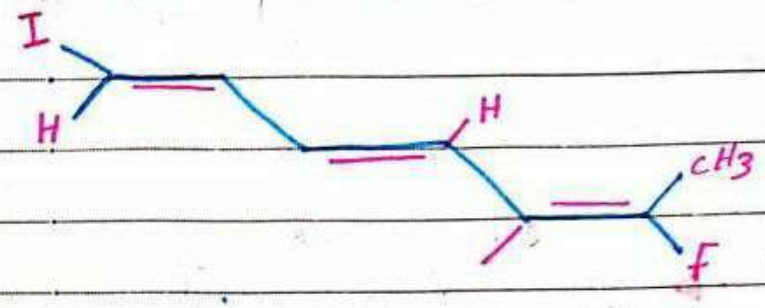
* C≡C : H

9)



1E,5Z - 1 fluro - 1 Bromo - 6 methyl oct 1,5 dienes.

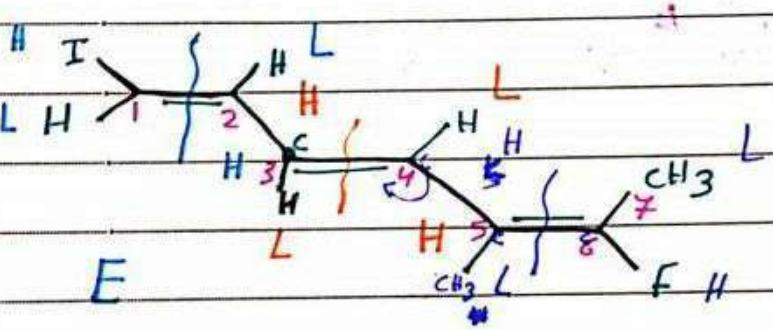
10)



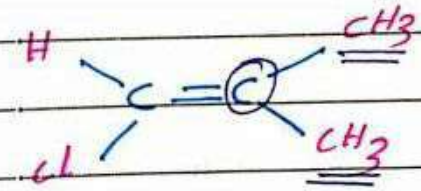
2 + 4 + 6 = 12

1 + 3 + 5 = 9

1E, 3E, 5E 1-Iodo-5methyl hept 1,3,5 trienes.



Note: cis, Trans } Geometric isomer.
2, E }

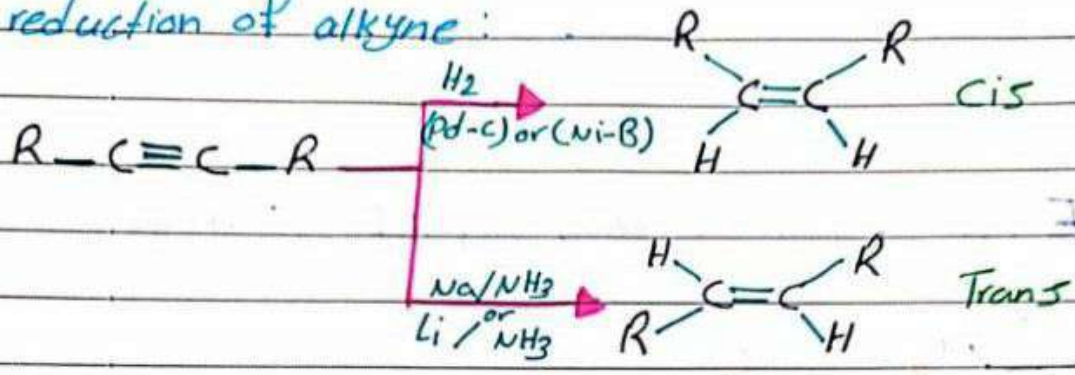


X No isomer

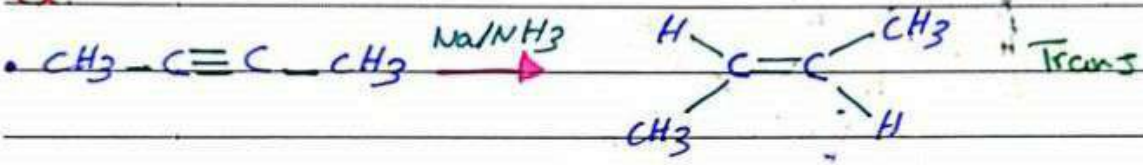
في حال تشابهت المجموعات المرتبطة في نفس C

- preparation of alkenes:-

1). reduction of alkyne:



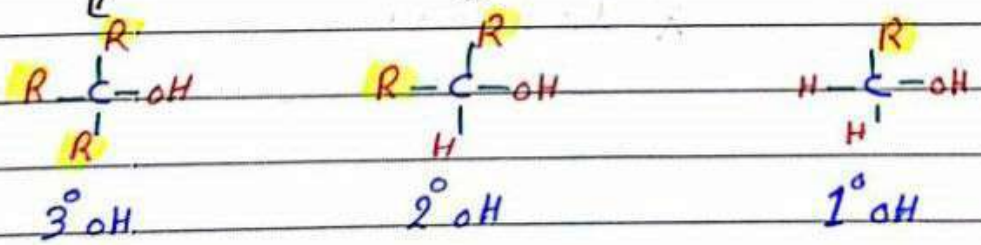
ex:



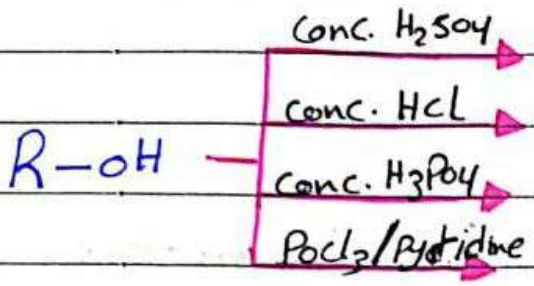
2) Dehydration of alcoholes: نزع جزيء ماء من الكحول

لما نزع جزيء ماء

Types of Alcoholes → due to the R



*How is the process of Dehydration done??



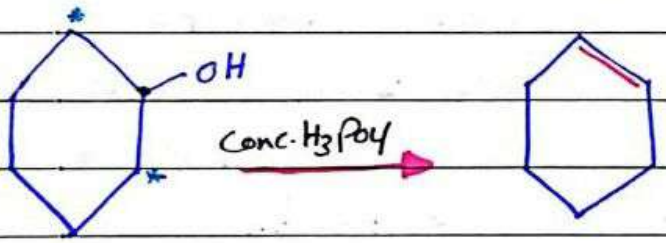
ex:

1) $CH_3-\overset{*}{C}H_2-OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2=CH_2$

• Define the carbon which associated with OH, then we remove H from the carbon that associated with it.

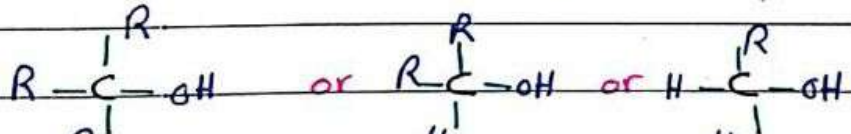
يتم تحديد الـ C المرتبطة بـ OH ثم نزيل H من الكربون المجاور لها. (الأصغر وعدداً)

2)



* which is easier in dehydration process?

أيهم أسرع في عملية النزع؟

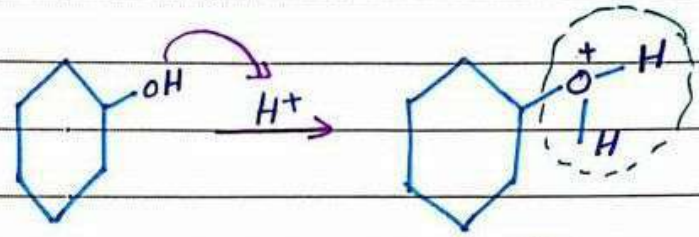


3°OH 2°OH 1°OH.

To answer it we should explain the mechanism of reaction.

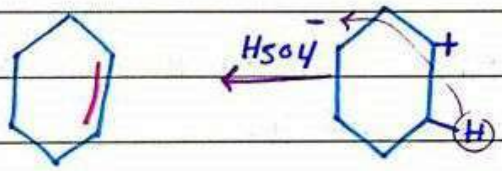
* Mechansim of Reaction :-

- $H_2SO_4 \longrightarrow H^+ + HSO_4^-$



G.L.G → good leaving group

$-H_2O$



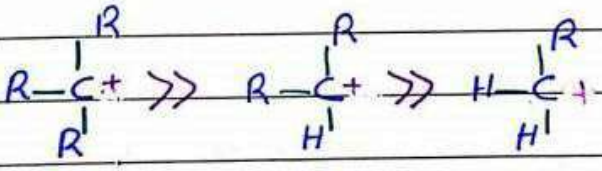
→ carbocation

* whenever carbocation is more stable the process of dehydration become more easy.

قدرت تكون carbocation اكبر تجعلها مستقرة

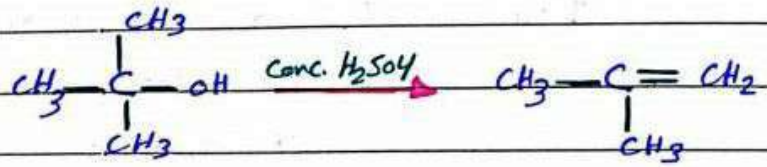
تكون عملية النزع تحدث.

Now we back to the previous question !!.



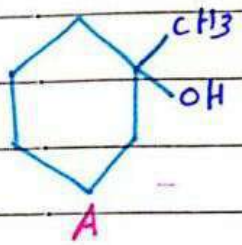
3° alcohole >> 2° OH >> 1° OH

ex:

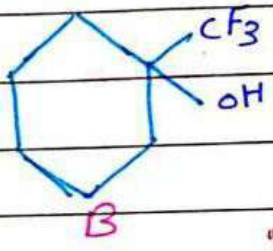


نحدد C الموجبة بـ OH ثم نأخذ H من أكبر مجموعة وتصبح بره

which of the following is easy to be deydration ??

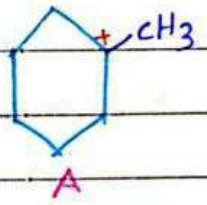
1) 

A

or 

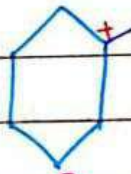
B

"In your subconscious mind"
باللغة الباطنة



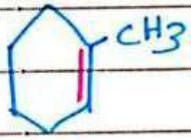
A

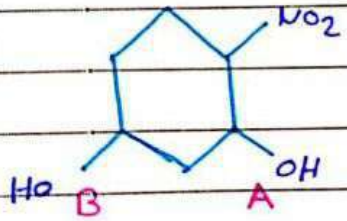
>>



B

The question transfer to
which compound is more stable ??



2) 

بعتقد B لانه بتحول carbocation اسرع هيبة بسبب
محبوبة withdrawing باتجاه A اقوى
باتجاه تكون شريك في علة الرنين

3)

3) Dehydrohalogenation of alkyl halide using KOH/alcohole.

HX

1) $CH_3-CH_2-Cl \xrightarrow{KOH/alc.} H_2C=CH_2$

2) $CH_3-CH(Cl)-CH_2-CH_3 \xrightarrow{KOH/alc.} CH_3-CH=CH-CH_3$

- we remove the hydrogen from the group which is has more substituted

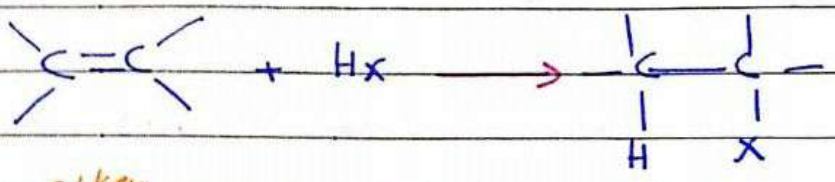
in other word the group most alkylaled due to the rule of (Zaitsev Rule)

3) $CH_3-C(CH_3)(Cl)-CH-CH_2-CH_3 \xrightarrow{KOH/alc.}$

$CH_3-C(CH_2)=CH-CH_2-CH_3$

1. electrophyilic Addition:

a) HX. hydrogen halide

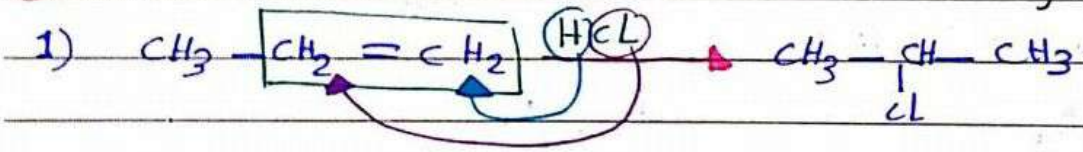


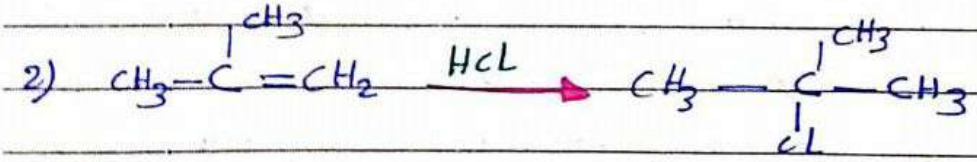
alken

Due to "Markeovnikov"

The rule states that with the addition of HX to an alkene the hydrogen-H gets attached to the carbon with more hydrogen substituents, and the halide (X) group gets attached to the carbon with more alkyl substituents.

ex:

1) 

2) 

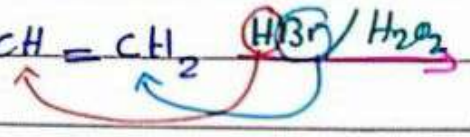
* Anti-Markovnikov reaction.

a) HBr / H_2O_2 → peroxides

only HBr

$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CH(Br)-CH_3$ Due to Markovnikov

But If we add HBr/H_2O_2 it become Anti-Markovnikov .

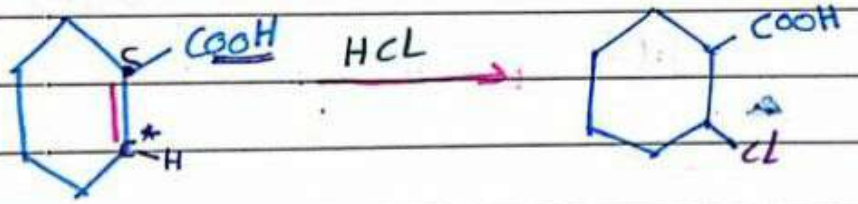


In Anti-Markovnikov the halogen gets attached with more hydrogen substituents and the halhydrogen gets attached with alkyl group

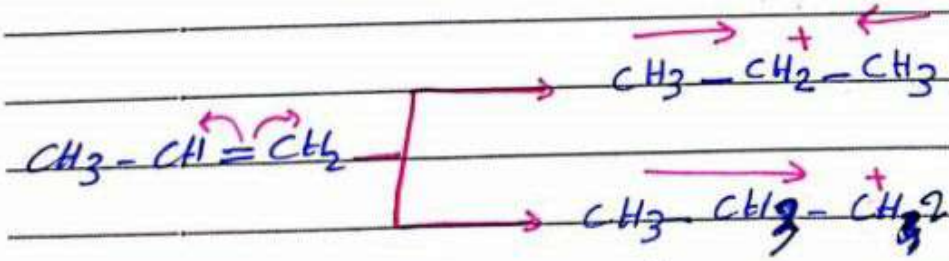
عكس ماركوفنيكوف أي أنه الهالوجين X يرتبط بالكربون الذي تحتوي على هيدروجين أكثر في حين أن الهيدروجين يرتبط بالكربون التي تحتوي على هيدروجين أقل

It's called (peroxide effect)

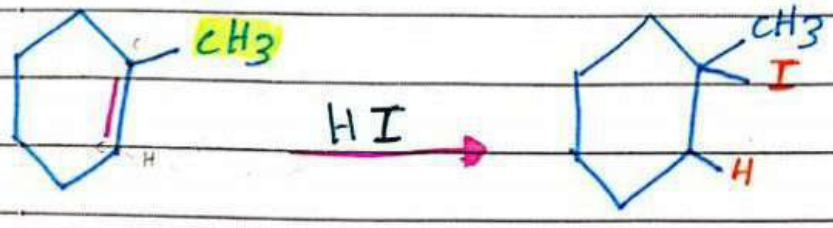
b) withdrawing group.



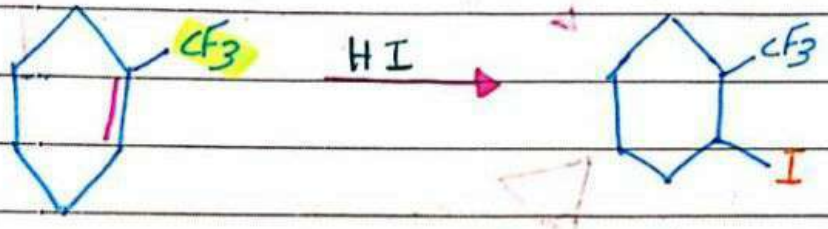
ننظر للرابطة الثنائية وش أي منها تحتوي على H أكثر مع الانتباه أنه * تحتوي على H أكثر كون أنه C التي بالأعلى X تحتوي على أي هيدروجين لأنه بسبب وجود المجموعة الساحبة COOH يصير Anti-Markovnikov.



* complete the folowing reactions :-

1) 

Markovnikov
CH_3 donat

2) 

Anti-Markovnikov.
CF_3 withdrawing.

2. Br_2 / cCl4 " anti addition".

$C=C \xrightarrow{Br_2/ccl_4} C(Br)-C(Br)$

- كل ذرة C تحتوي على ذرة لذلك حدث anti-addition بسبب steric hindrance الحالة الفراغية . Br بسبب كبر حجم

3. wader / H^+ → acidic medica

* بدون H^+ لا يتم التفاعل.

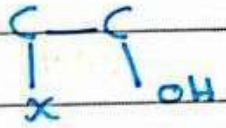
$C=C + H_2O \xrightarrow{H^+} C(OH)-C(H)$ alcohole.

$CH_3-CH=CH-CH_3 + H_2O \xrightarrow{H^+} CH_3-CH(OH)-CH_2-CH_3$

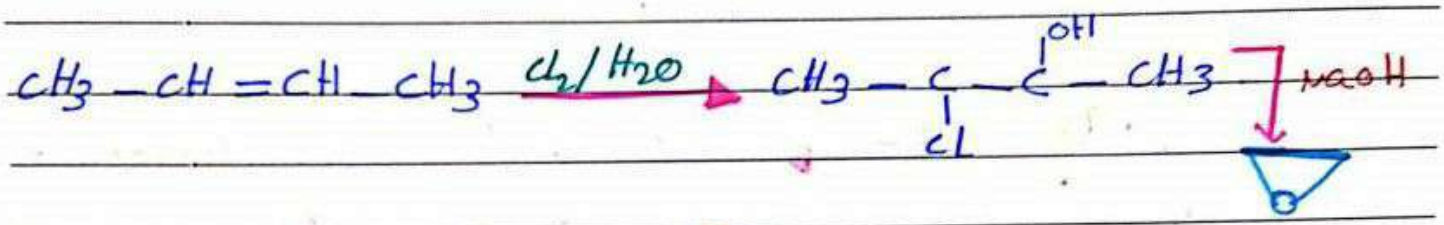
4. halohydrine formation.

by X_2 / H_2O

* halohydrine



halide hydroxy



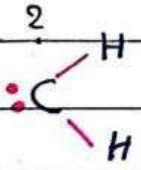
halohydrine $\xrightarrow[\text{or NaH}]{\text{NaOH}}$  epoxide

5. alkene with carben.

* How we get carben ?

- by diazomethan

* what is the structure of carben ?

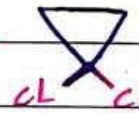


$CH_2N_2 \xrightarrow[\text{Light}]{h\nu}$:CH(H) • carben

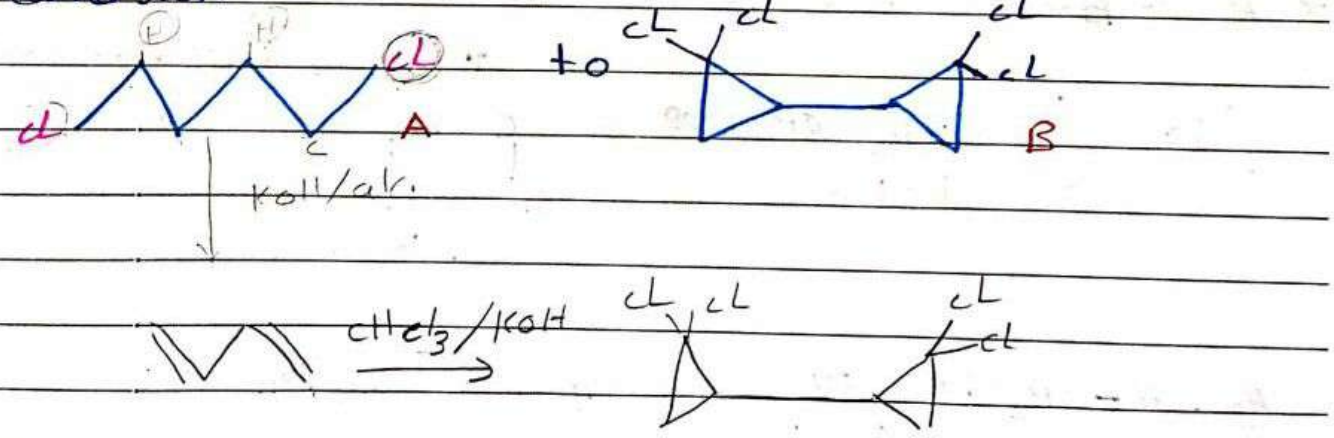
$CHCl_3 \xrightarrow{KOH}$:C(Cl)(Cl) • substituted carben

[chloroform

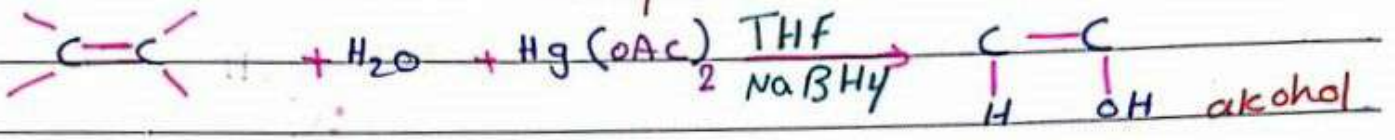
* $CH_2=CH_2 \xrightarrow[\text{Light}]{CH_2N_2}$  cyclopropan

* $CH_2=CH_2 \xrightarrow{CHCl_3/KOH}$  substituted cyclo propan

* conversion



6. oxymercuration - demercuration



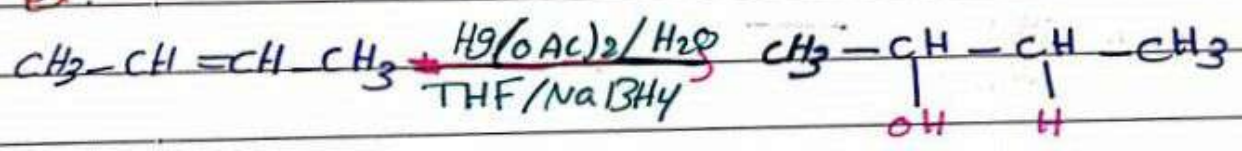
" Markovinkov rule "

* THF:
Tetrahydrofuran.

* NaBHH:
sodium borohydride.

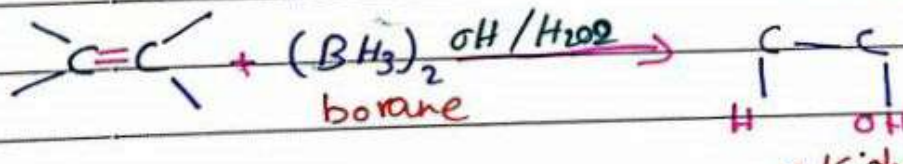
* كانه بيم بضافة الماء صب قاعدة وبكونيكفا .

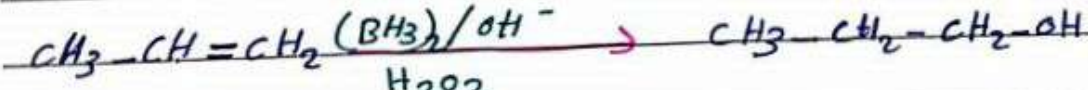
ex:



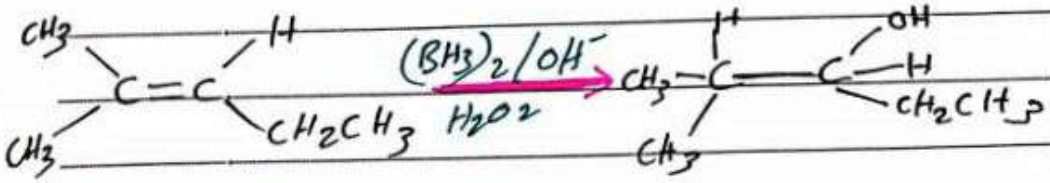
7. Hydro boration oxidation reaction:

∴ H_2O_2 → "Anti Markovinkov"





from book:



• oxidation of alkenes:

Type of oxidizing agent depend on Type of substituted alkene

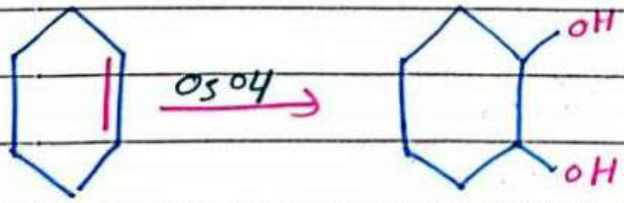
oxidizing agent

- Mild
  - O_3 "Ozonlysis"
  - cold KMnO4, OsO_4, HCOOOH
- strong
  - hot KMnO4 or $K_2Cr_2O_7$

*Glycol formation:

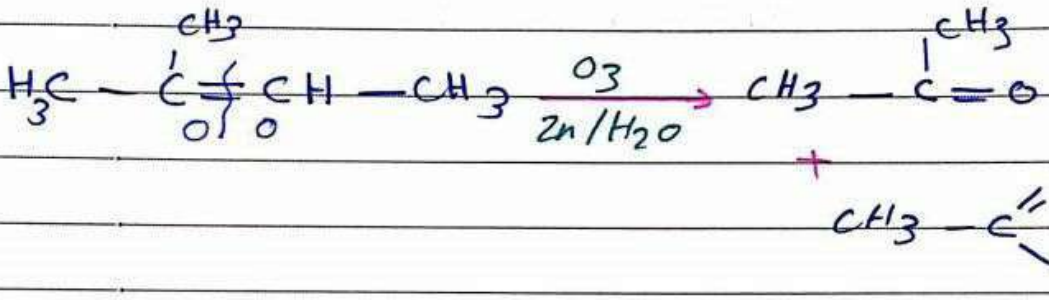
• يختلف المركب حسب الطول المذكور

$$C=C \xrightarrow[\text{or } OsO_4 \text{ or } HCOOOH]{\text{cold KMnO4}} \underset{OH}{\overset{}{C}}-\underset{OH}{\overset{}{C}}$$



* Ozonlysis :-

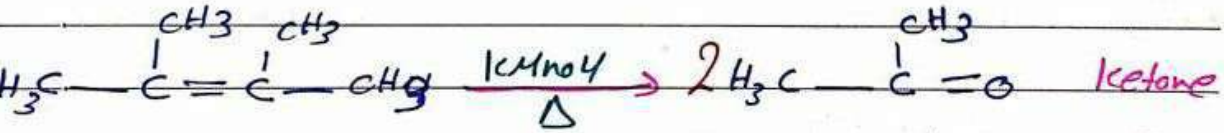
$C=C \xrightarrow[Zn/H_2O]{O_3}$ aldhyde or ketone



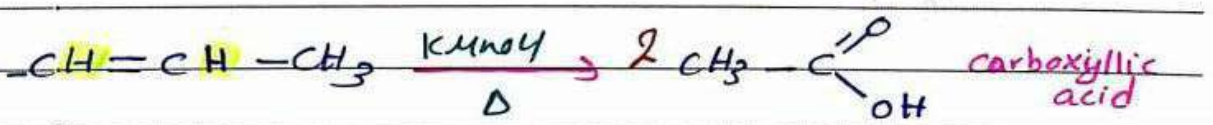
• Strong oxidizing agent :

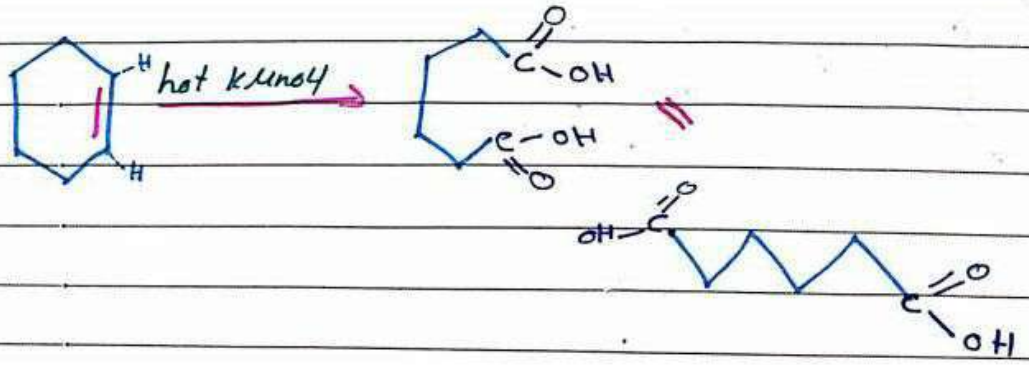
$C=C \xrightarrow{\text{hot } KMnO_4}$ ketone or carboxyillic Acid

- If there isn't any H on double bond give us ketone.

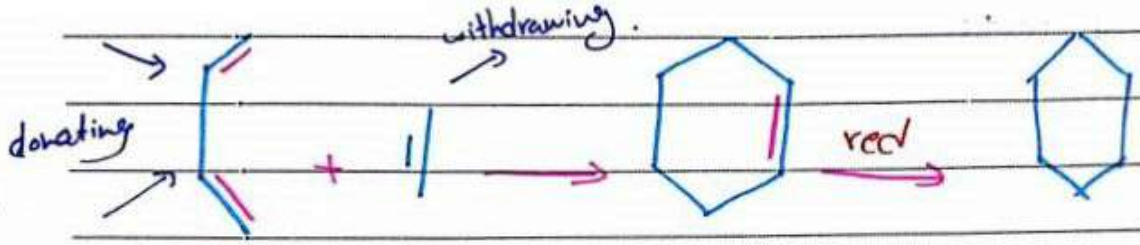


- اذا لم يوجد اي H على C يعطينا كيتون



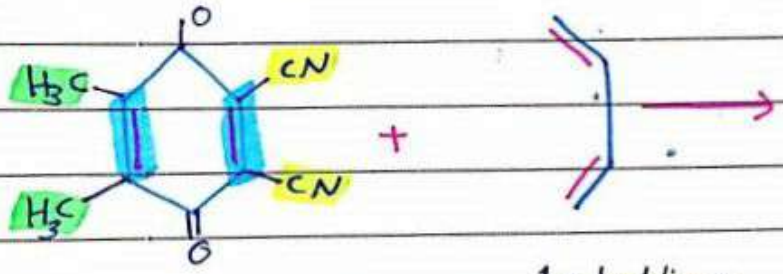


* Diels Alder Reaction "cyclohexen" → "cyclohexan"

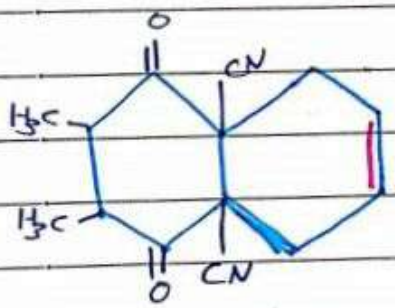


1,3 butdiene

Alkene
donate group
withdrawing group

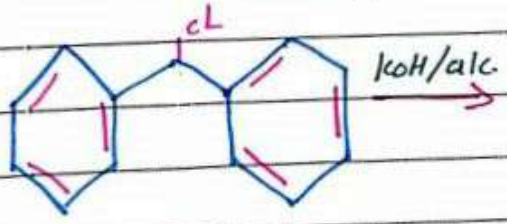


1,3 butdione

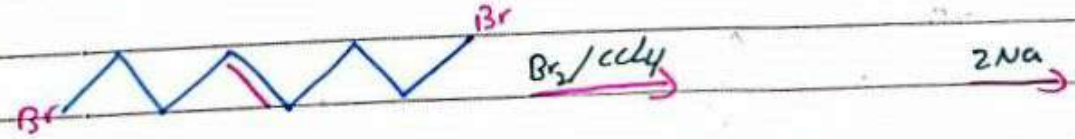


Complete the following reactions :-

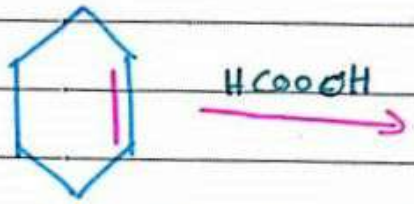
1)



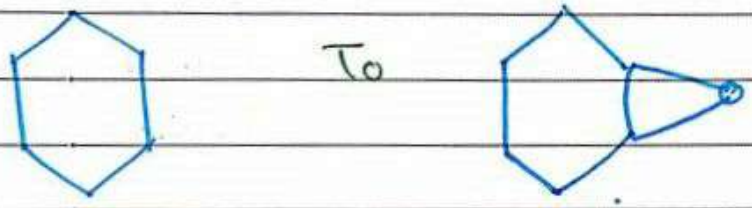
2)

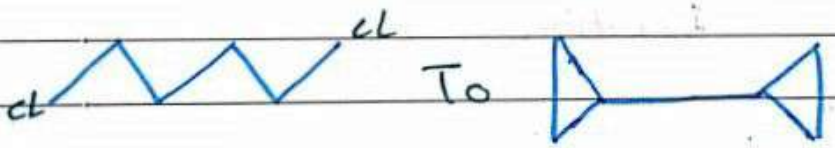


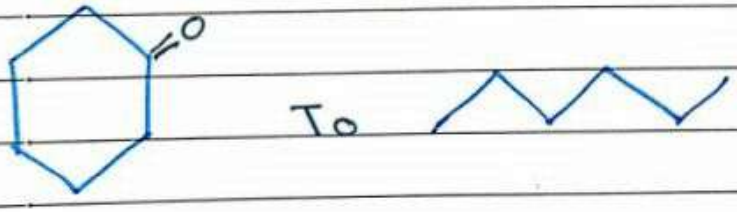
3.



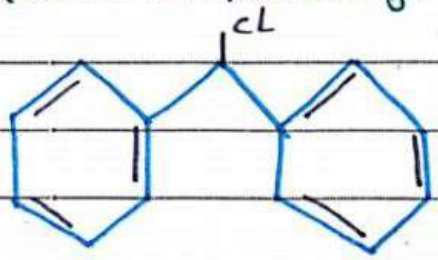
Conversion :-

1) 

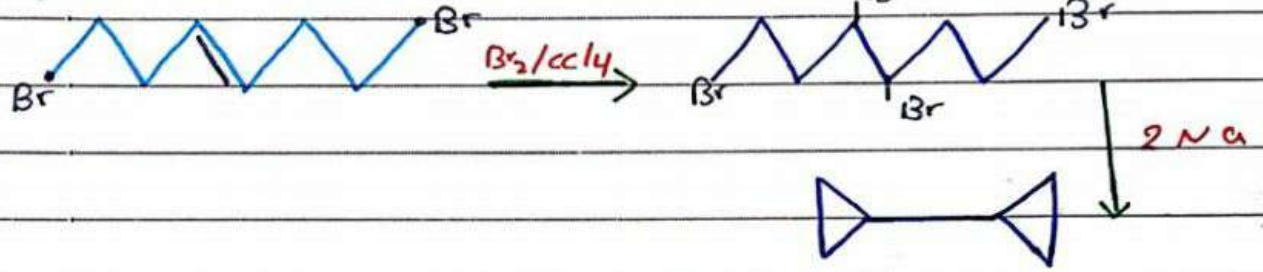
2) 

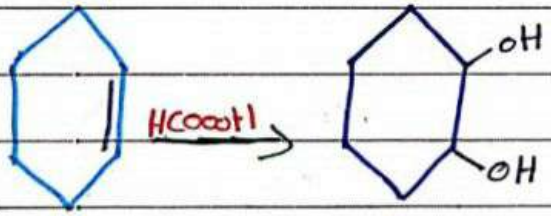
3) 

* complete the following reaction :

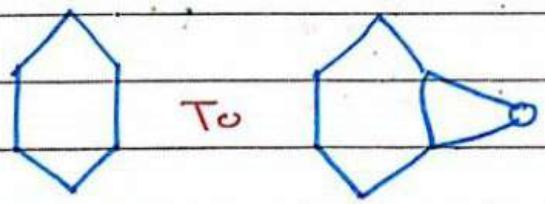
1) 

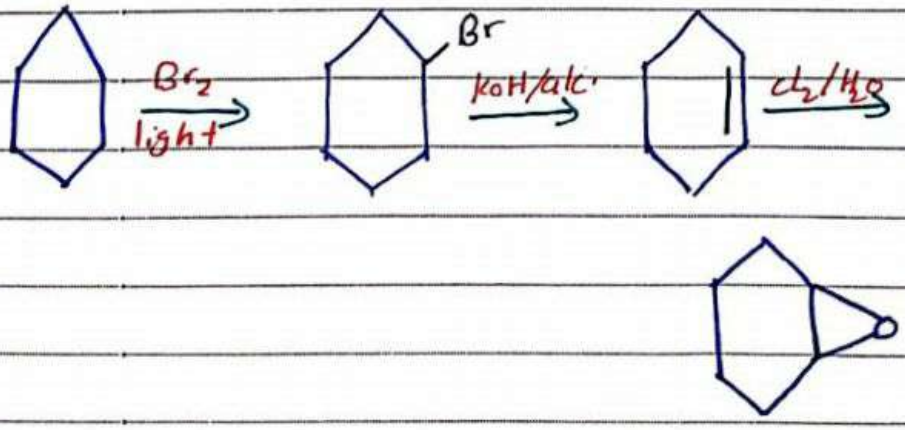
KOH/alc. → No reaction.

2) 

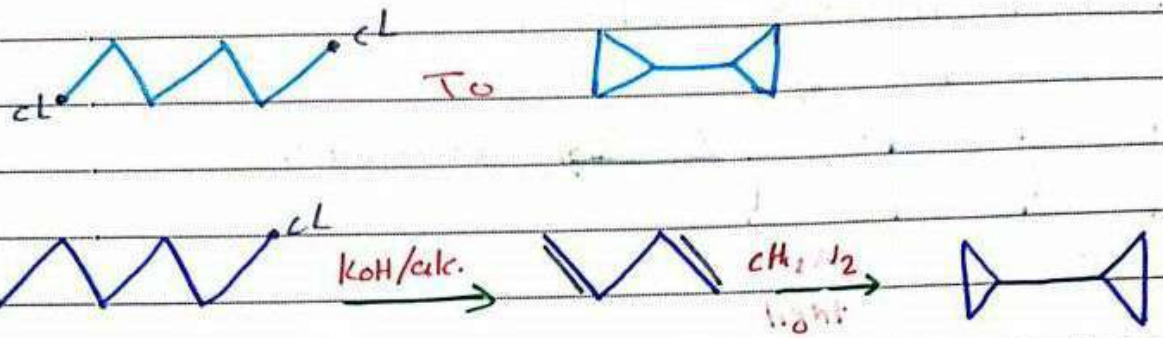
3) 

* conversion of~

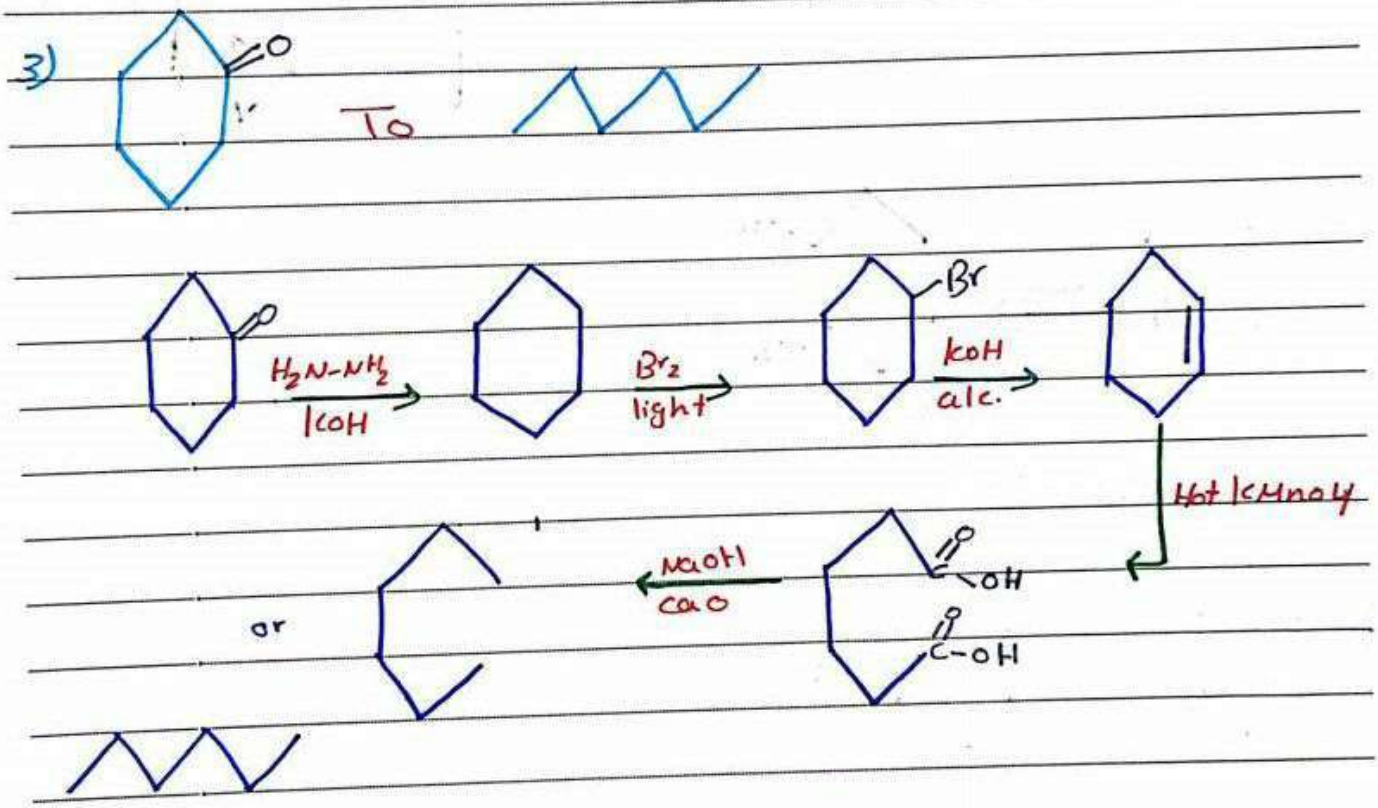
1) 



2)


Cl
Cl
To
Cl
Cl
KOH/alc.
CH_2I_2
Light

3)


O
To
H_2N-NH_2
KOH
Br_2
light
Br
KOH
alc.
Hot KMnO4
NaOH
CaO
OH
OH
or

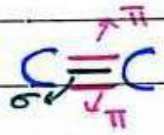
Alkynes

12/4/2020 Sunday
8th electronic lecture.

Alkynes :-

The compound that contain Triple bond and the general formula is

C_nH_{2n-2}



alkyne.

Types of Alkyne

Terminal Alkyne

$H-C\equiv C-R$

* contain Hydrogen
H يحتوي على هيدروجين

non terminal Alkyne

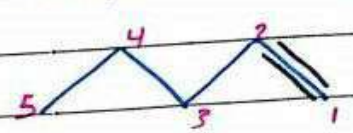
$R-C\equiv C-R$ or Ar

* don't contain Hydrogen
لا يحتوي على هيدروجين H.

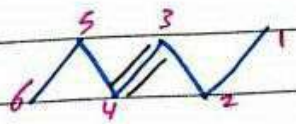
- Nomenclature of Alkyne.

alkane → alkyne

يجب توضيح مكان الرابطة.



pentyne

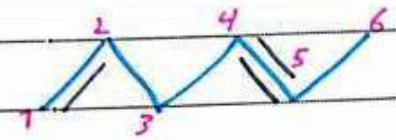


hex-3-yne or 3-hexyne.

* If the compound contain double and Triple bond we put
* double bond then triple bond.

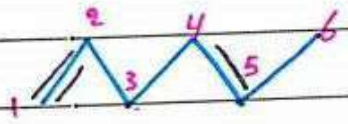
enyne ≠ yneen

ex:



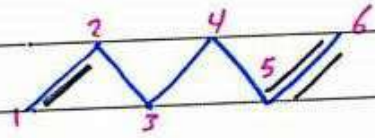
* لم تتساوى علاوة الترقيم نرقم من الأقرب

hexene-4-yne.



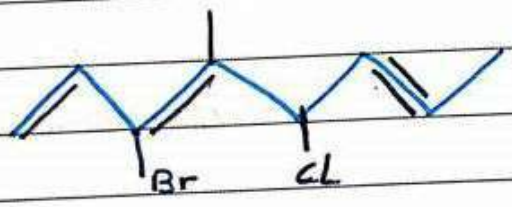
hex-4-en-yne

* في حالة تساوي الترقيم لـ double مع Triple فالأولوية لـ double bond

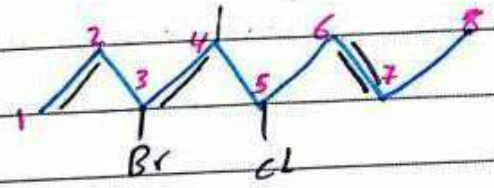


hexen-5-yne

ex:

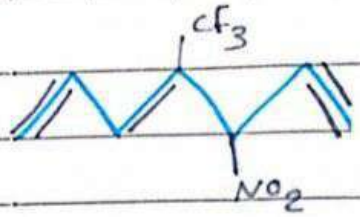


Sol.

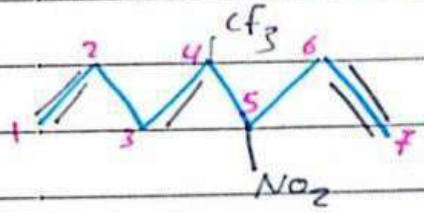


3-Bromo-4-methyl-5-chloro oct-1,3-dien-6-yne.

ex:



Sol.



4-trifluoromethyl-5-Nitro hept-3-en-1,6 diynes.

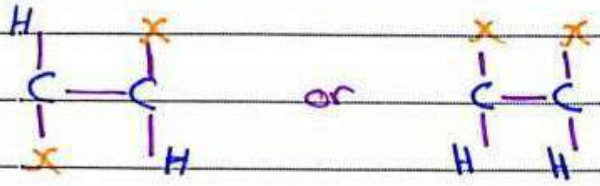
If the compound contain more than one triple bond we put:

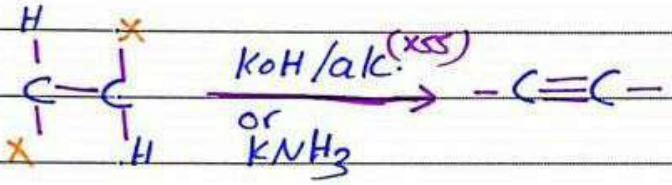
1 yne
2 diynes
3 triynes

Preparation of Alkynes

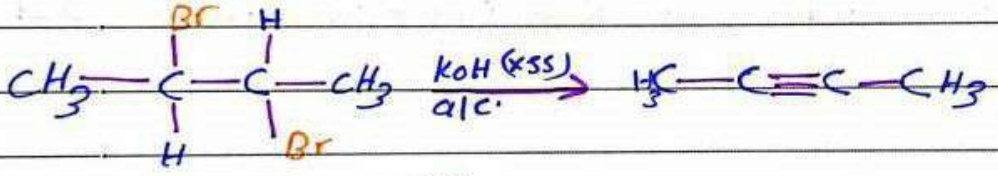
13/4/2020 Monday
9th electronic lecture.

1) Dehydrohalogenation of alkyl dihalide.





ex:)



2) Reaction of sodium acetylide with alkyl halide.

- we use it to produce (longer alkyne)

$$HC\equiv C-Na + R-X \longrightarrow HC\equiv CR + NaX$$

"sodium acelyide"

ex:)

$$HC\equiv C-Na + CH_3-CH_2CH_2CH_2-Br \longrightarrow$$

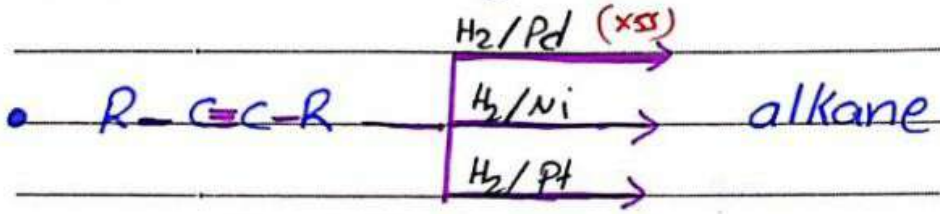
$$HC\equiv C-\underbrace{CH_3-CH_2-CH_2-CH_2}_{C_4H_9} + NaBr$$

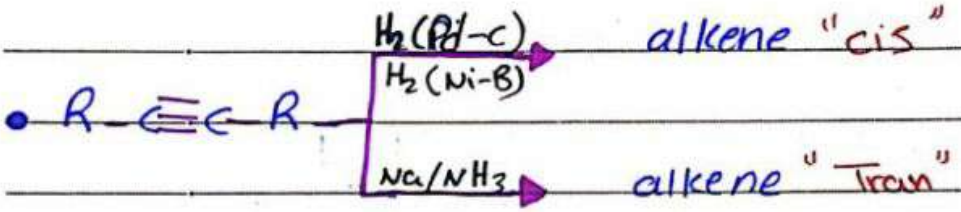
or

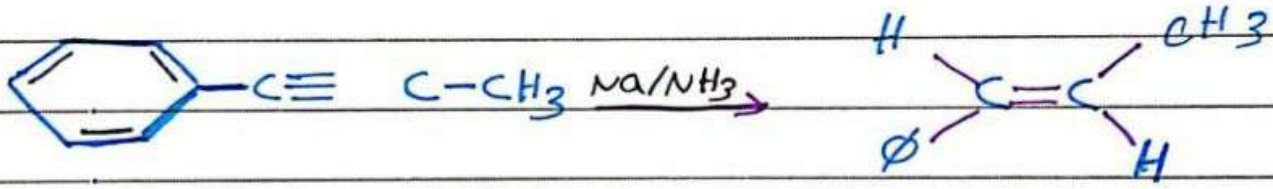
$$HC\equiv C-C_4H_9 + NaBr$$

Reactions of alkynes :-

1) reduction of alkyne

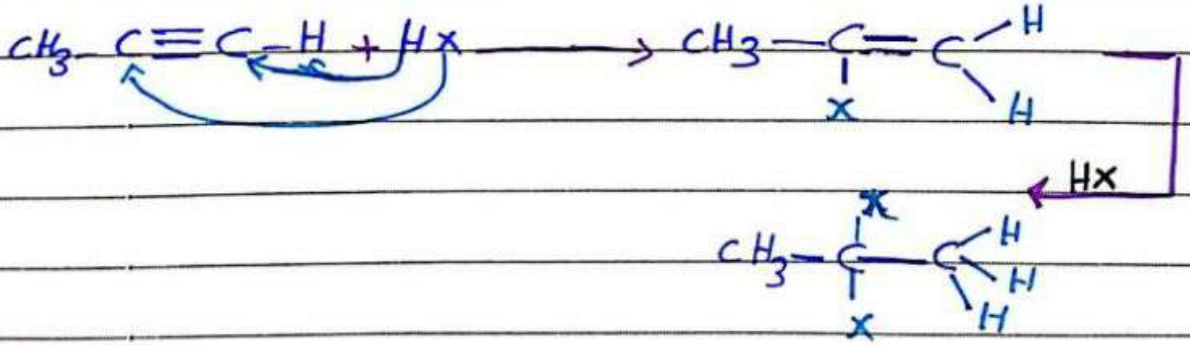


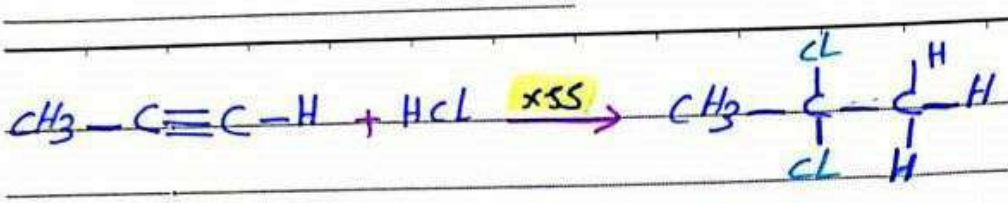




2) Halogenation of alkyne

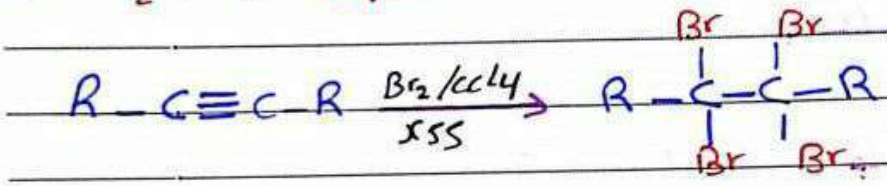
a) Hx "Markovenkove"



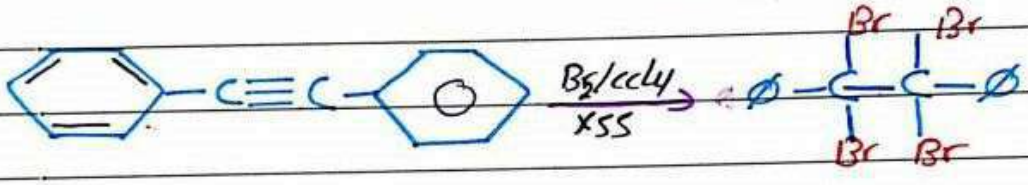


لحتما يكون xss كأنه أضفنا HX مرتين

b) X_2 (Br_2/ccl4)

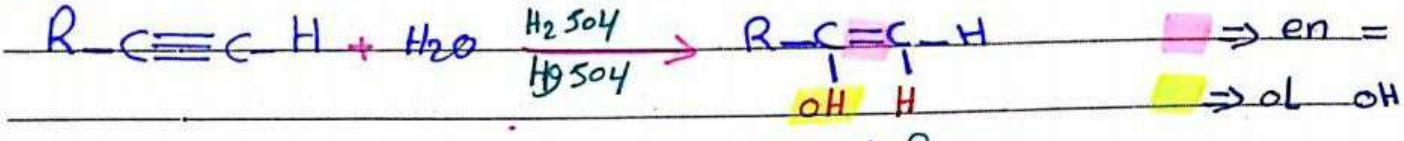


ex):



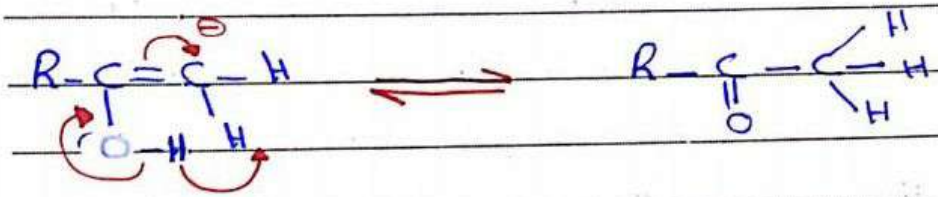
3) Hydrolysis of alkyne " hydration".

A) by $H_2SO_4/HgSO_4 + H_2O$ "Markovenkov"



⇒ en = ⇒ ol OH

enol form



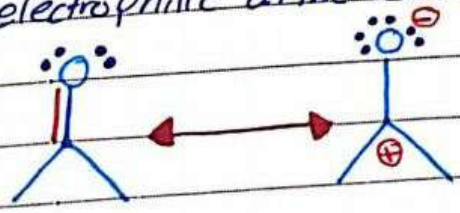
enol form Keto form

tautomerism = tautomerization

What is the difference between Tautomerism & reasonance?

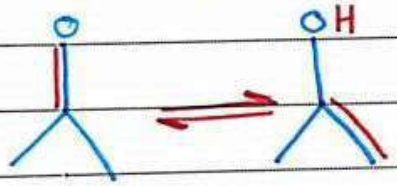
- Resonance structures are different representations of the same structure. But they differ in the arrangement of their lone pairs and double bonds.

In the figure below is acetone. Acetone can be represented by Two different resonance structures. They are useful for exploring the reactivity of a particular of a substrate. For example, In Acetone the resonance structure on the right suggests that acetone would be nucleophilic at the oxgen and electrophilic at the carbon.



- resonance: same structure - different representations.

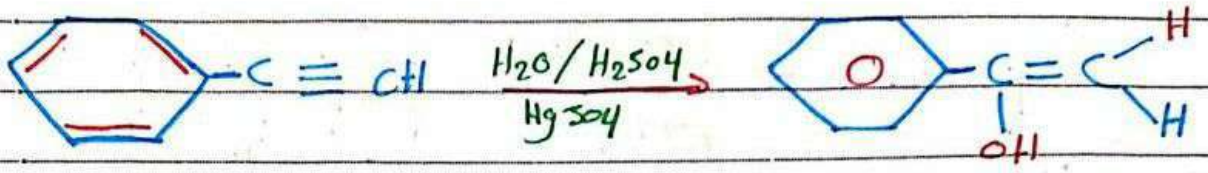
• Tautomerization involves a change in connectivity of the atom to yield two different constitutional isomers. Thus, tautomerization is an actual chemical reaction that can take place. The two tautomers will have different reactivity, boiling points, melting points, etc. They are two unique molecules. In the figure below, I drew the ketone and enol forms of acetone. In order to go from keto to enol, I have to change the connectivity of the atom (break sigma bonds).



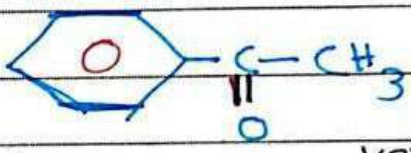
• tautomers: - Two different structures
- constitutional isomers.

- I use a double headed arrow for resonance, and I use equilibria arrows for tautomers.

ex)

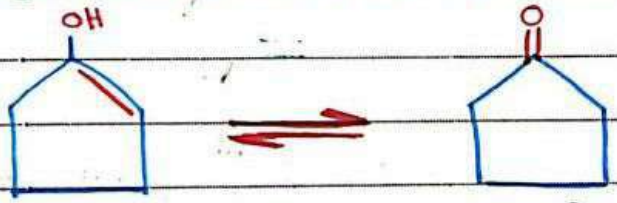


enol form

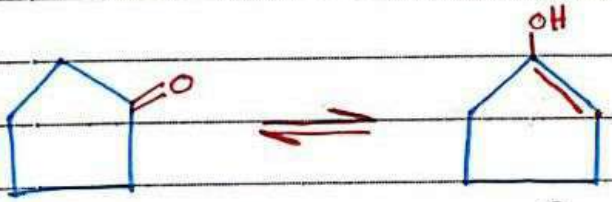


keto form

write the tautomerism for the following compound:-



enol form. keto form.

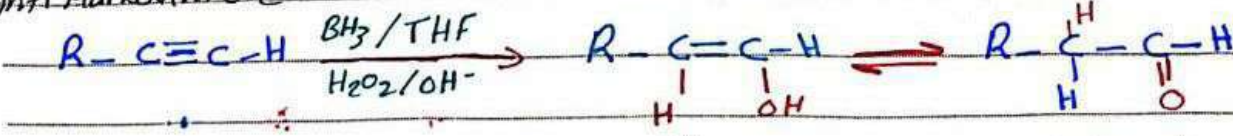


keto form enol form

B) By BH_3 / THF Hydroboration - oxidation of alkyne.

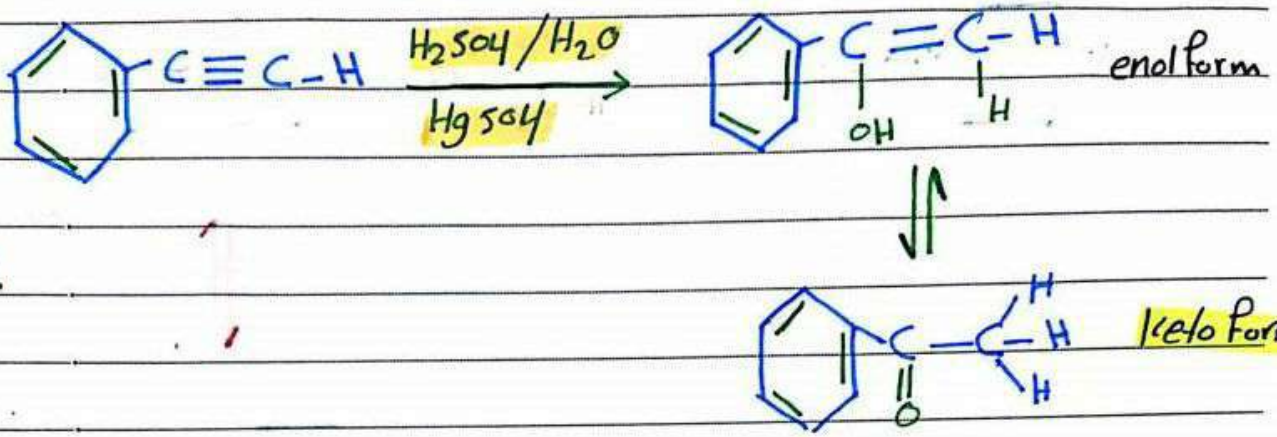
H_2O_2 / OH^-

"Anti Markovinkove".

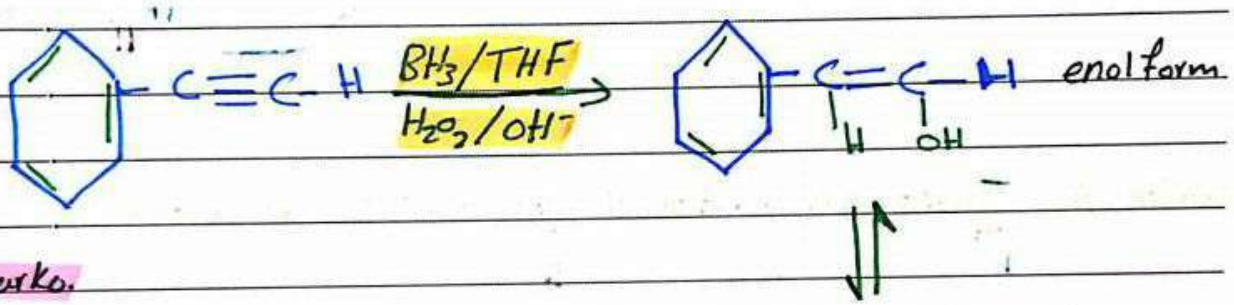


enol form Aldehyde

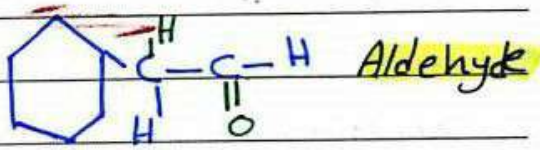
Aldehyde

A) 

Markо.

B) 

Anti Markо.



4) oxidation of alkyne.

- Depends on the Type of alkyne if its terminal or non terminal

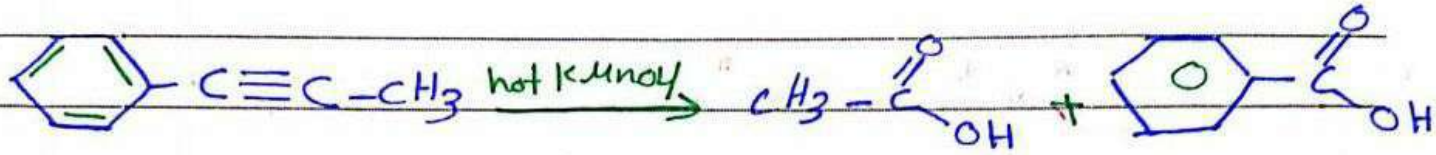
- $R-C\equiv C-H \xrightarrow[\text{or } O_3]{\text{Hot KMnO4}} CO_2 + C.A$ *C.A → carboxlic Acid.

"Termined"

- $R-C\equiv C-R \xrightarrow[\text{or } O_3]{\text{Hot KMnO4}} 2\ C.A$

"non Terminal"

Ex) * $CH_3-C\equiv C-CH_3 \xrightarrow{\text{hot KMnO}_4} 2\,CH_3-COOH$

* 

* اذا اختلفت المجموعات نفس كربوسيل شيء لكن واحدة عزيزا .

!!

Stero chemistry

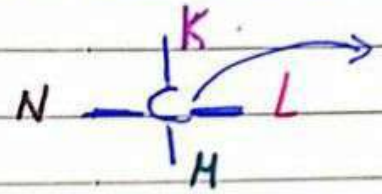
18/4/2020 Saturday

11th electronic lecture.

Branch of chemistry concerned with the arrangement of atoms or groups in the space.

"chiral center" or "chirality" or "sterogenic center".

- The carbon atom bonded to different four groups.



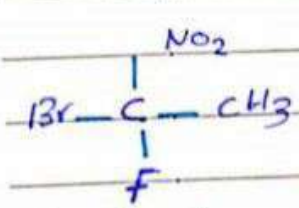
chairl carbon

sp^3 → just in singl bond sigma.

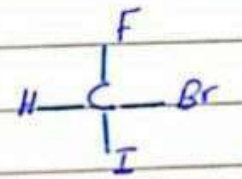
If there's douple bond it's A chairl.
or Tripl.
or 2 same group

- If there isn't chairl carbon we named A chairl carbon.
- To get the isomer for the chairl carbon: 2^n

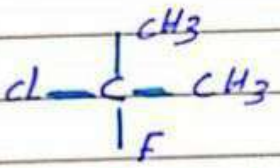
n: the number of chairl atom in the compound.



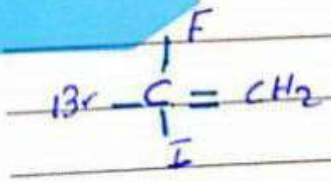
Chiral carbon



chairl carbon.

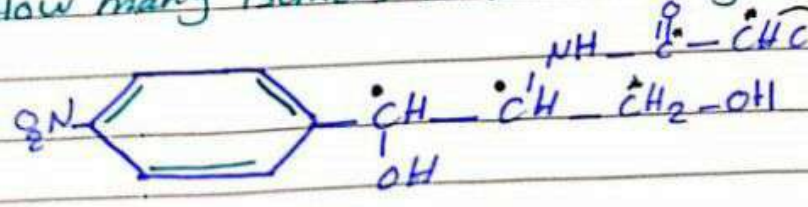


A. chairl carbon.



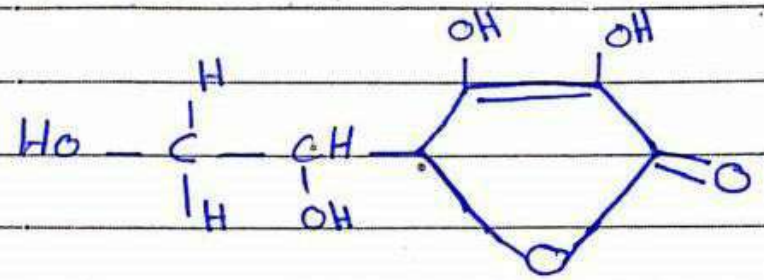
A chairl carbon.

How many isomers in the following compound...



$2^2 = 4$ isomer.

How many isomer in the following compound?



$2^2 = 4$ isomer.

* The compound that contain chairl center has "Optical activity" speciality.

• optical activity: The ability of atom to rotate polarized light toward left or right

• If the polarized light was to the left we called it levorotatory "L"

• If the polarized light was to the right we called it "Dextro rotatory" "D"

- To determination the configuration of the compount that has chairl center $\xrightarrow{\text{has}}$ chairl center.

If the right deviation rate is equal to the left deviation rate we called this cas "optical Inactivity".

$D = l$

zero

optical inactivity.

complete of stereochemistry 18/4/2020 St.
12th elec. lec.

To determind the configuration of the compound that has chairl center.

- has to contain chairl center .
- Atomic number
-) with clockwise (counter clock wise

R S

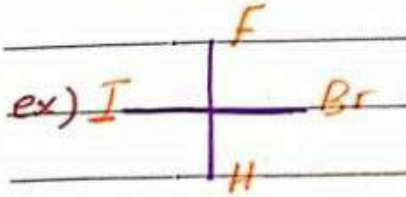
we have two ways to determind the configuration of the compound tha has chairl center.

Fisher projection. Tetrahedral

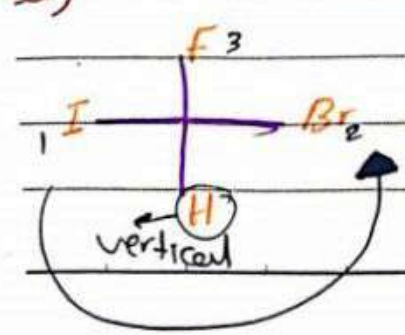
Fischer projection:-

- chiral center.
- sequence Rule. (A.N) ترتيب المجموعات على Atomic.no
- The smallest group should be at the vertical otherwise the configuration convert to (R→S) (S→R)

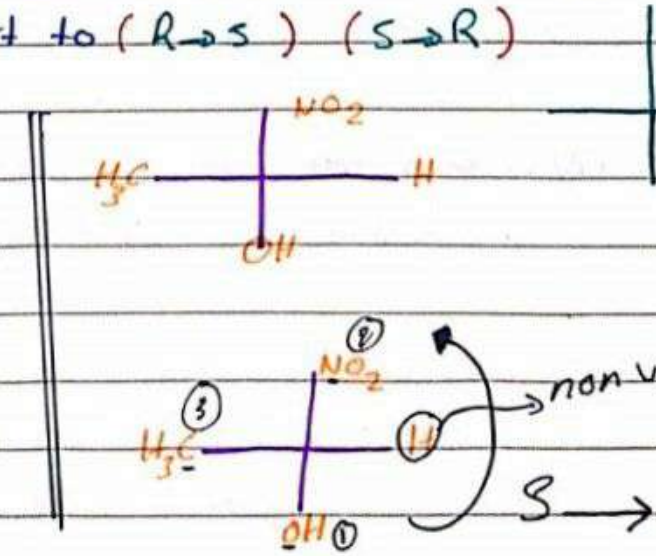
ex)

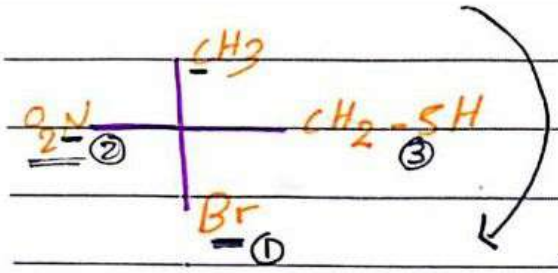


sol)



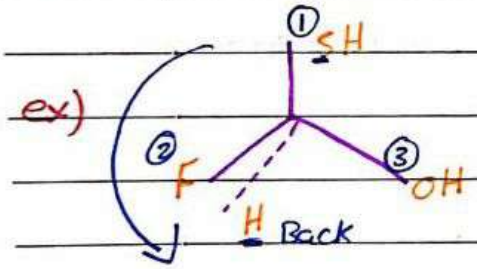
S

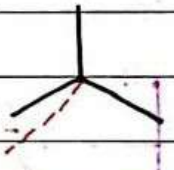




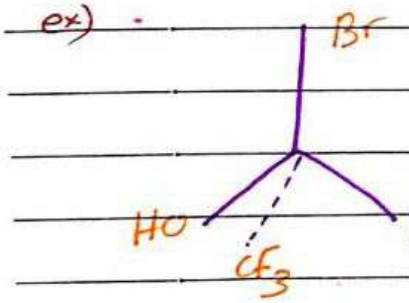
2 Tetrahedral :-

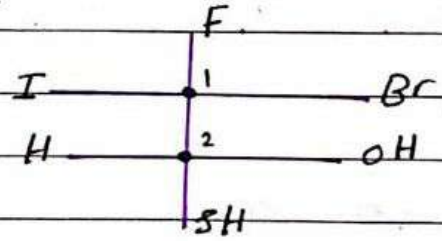
- Chiral center.
- sequence Rule
- The smallest group should be at the back otherwise the configuration convert to the (R→S), (S→R)

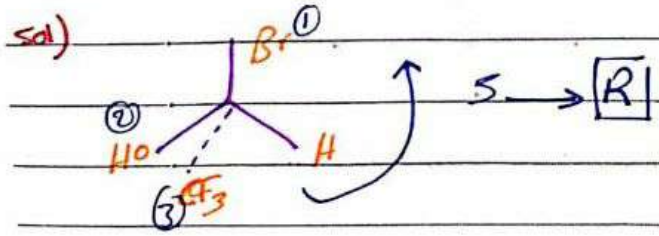


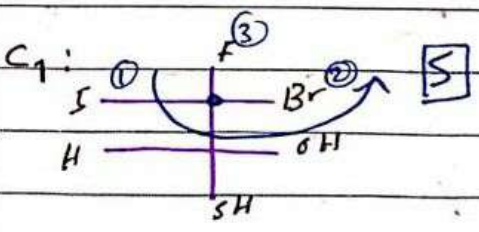


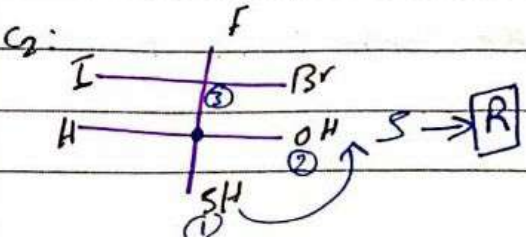
If the compound contain more than one chairl center











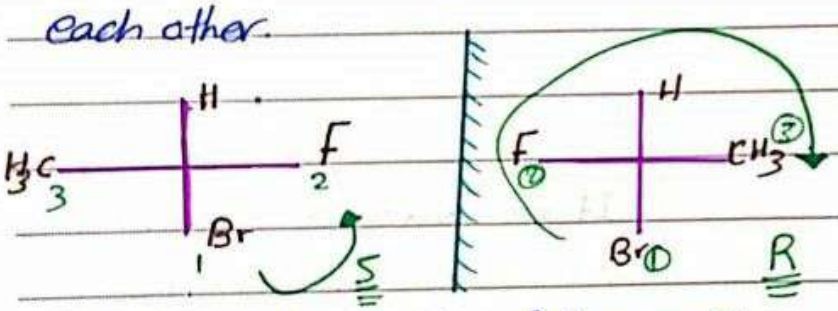
• Stero isomer.

The compound that have the same molecular form but different in the arrangement of the atoms in the space.

Stero isomer

Enanuomer

- The stero isomer compound which are mirror image to each other.

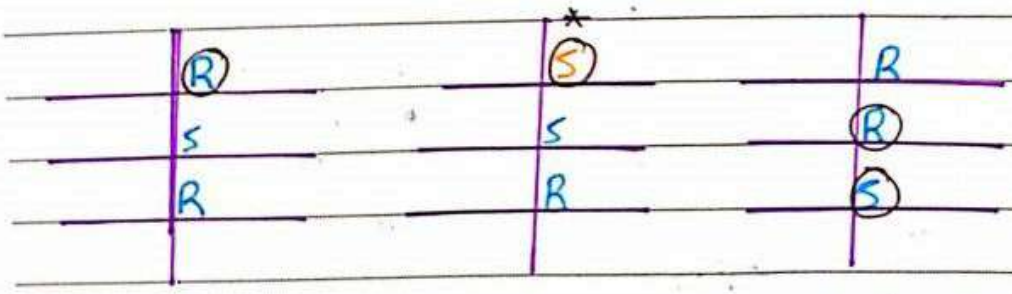


" Racemic Mixture" or " Racemat" optical Inactive.

Diasitomer

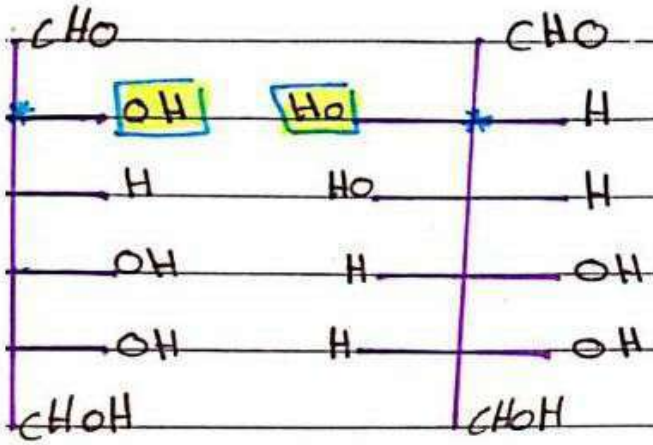
- The isomer compound different at least in one of chiral configuration.
- not mirror image.

Diastomer :-



If the change in Diastomer just in one chiral center we called it " epimer".

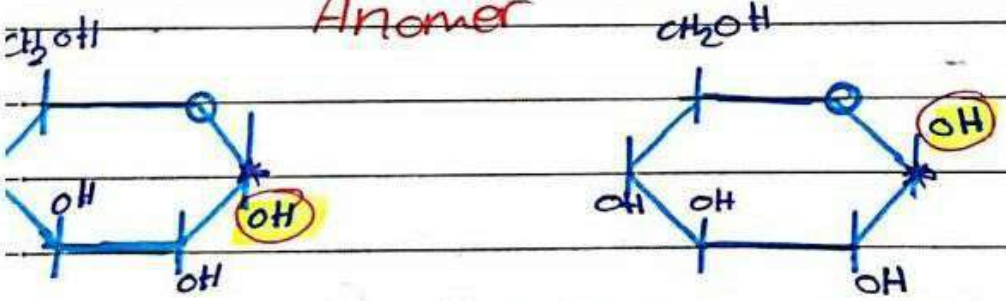
epimer.



rose D-Mannose.

is aspecial case of epimer we called it "Anomer" for sugar.

Anomer

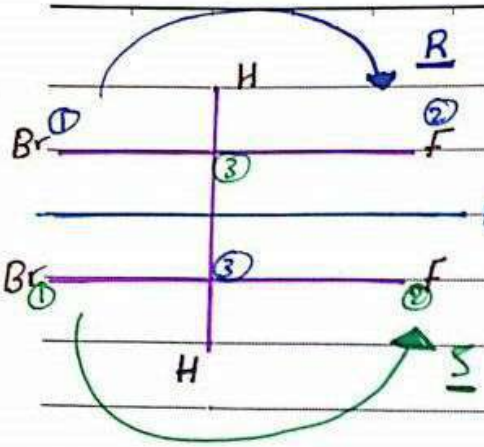


X-glucose β-glucose.

compound:

mpound that have chairal center and plane Symmtry ut the compound in to two super imposed part.

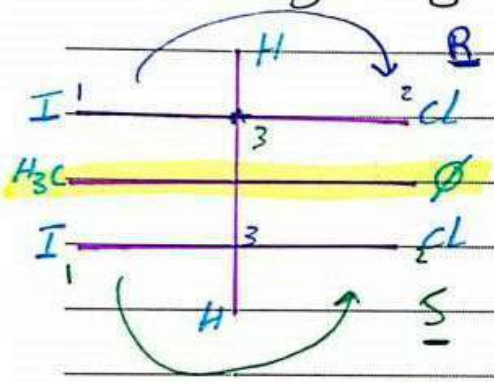
مركبات تحتوي على كربون chair/ وهو مثل الذي نقسم اوكيد لقسمين متماثلين



Note: ∵ S, R Parallel // So its Inact.

optecally Inactivity.

• The plan symmetry maybe in the same compound or outside.



R // S

optecally Inactivity.

* If the compound contain Two chairl center and ~~each~~ one of them is RR, SS we called it Erythro.

RS, SR Thero.

R_X

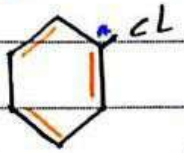
Alkyl Halide

$\overset{*}{C}H_3-Cl$

sp^3

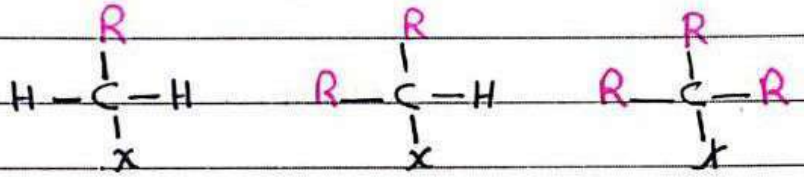
Ar_X

Aryl Halide.



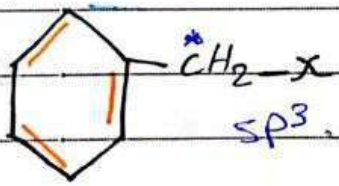
sp^2

- Types of alkyl halide :-

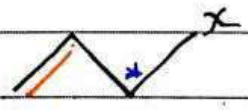


1° Rx $\quad$ 2° Rx $\quad$ 3° Rx

- special of alkyl halide :-



sp^3.

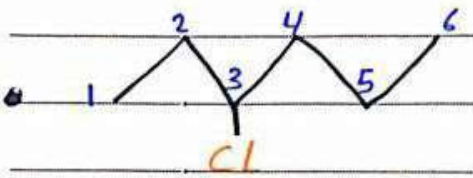


sp^3

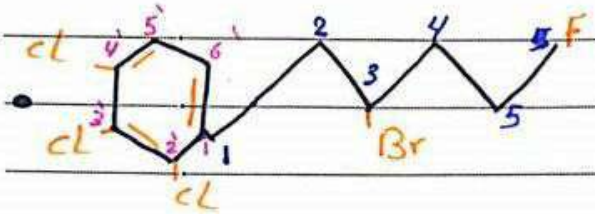
Benzyllic halide $\quad$ allylic halide.

- Nomenclature of alkyl halide :-

1. we consider the halide as substituted and take the less possible number.



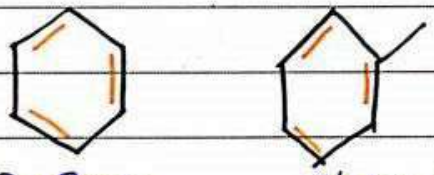
3- chloro hexane.



1-(2',3',4' tri chloro phenyl) 3-Bromo-5- flouro pentane.

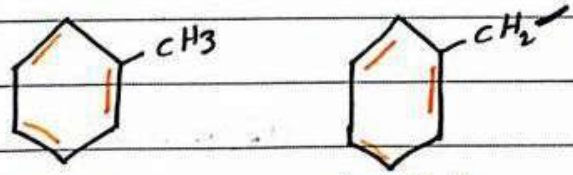
Note :-

- If the benzene ring, present as substituted. we named phenyl.



Benzene Phenyl.

- If the Toluene ring present as substituted we named benzyl.



Toluene benzyl

• preparation of alkyl halide :~

1- Halogenation of alkane.

2. Halogenation of alkene

Hx "Markovenikov"

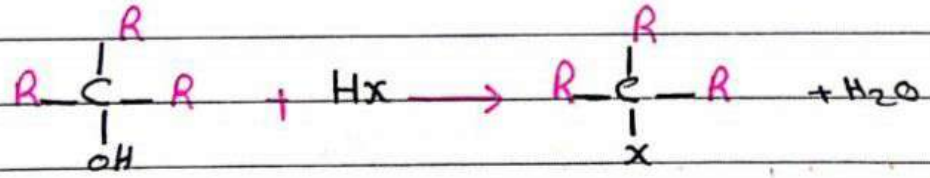
X_2/ccl4 , Br_2/ccl4 "Anti addition".

3. Halogenation of alkyne. !

xss Hx

xss X_2/ccl4

4. From alcohol.



3° alcohol.

• $SOCl_2$: Thionyl chloride.

• : pyridine.

1°, 2° alcohol $\xrightarrow[\text{  }]{SOCl_2}$ R-Cl alkyl halide.

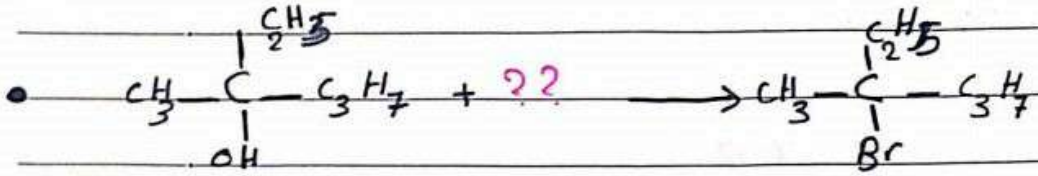
• we can exchange $SOCl_2$ by PBr_3 Tri bromo phosphine

• If we used $SOCl_2$ yidde alkyl halide as R-Cl, But If we used PBr_3 → R-Br Due to the regent we used.

$-PBr_5$

$-PCl_3$

$-PCl_5$



?? ⇒ HBr. Because it give us 3° alkyl halide.

15th electronic lecture.

Reactions of alkyl halide:-

1- Wartz Reaction.
2- Corye hous Reaction } in preperation of alkane.
3- Grignard Reaction
4- Frewnd Reaction. → in cycloalkane.
5- Substetution.
6- Elimmanation.

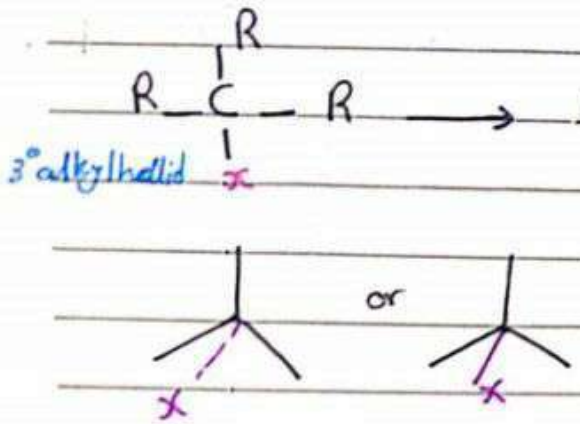
5- Nucleophyllic substitution SN

SN^1

- unimolecular Nucleophyllic substitution
- happened in 3° R-X and benzyllic halide also allyllic halide in Two steps.

SN^2

- Bimolecular Nuclophyllic substitution.
- occure in 1° R-X and 2° R-X
- just in one step



• Mechanism S_N1

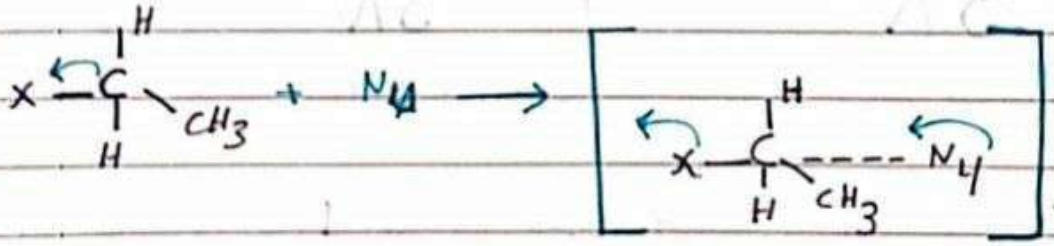
R
R – C – R
+
sp^2
Planer Triangle

Nu: Nucleophyllic.

50% inversion (نكس) 50% retention (نفس)

∵ produce 50% inversion and 50% retention so S_N1 optical inactive.

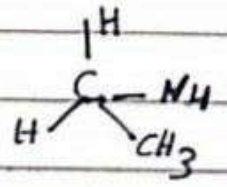
• The mechanism of S_N2



sp^3
Tetrahedral

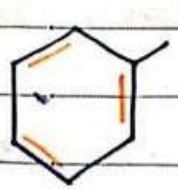
∵ yield 100% inversion so the compound is optical activity.

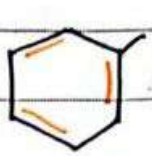
• intermediate that at the same time of Exit of halide the Nu enters.

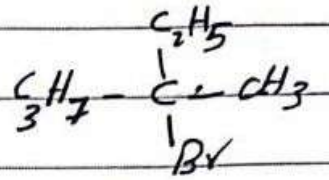


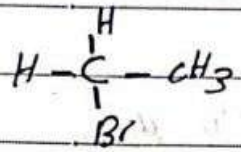
100% inversion

which of the following compound undergoes SN^1 reaction?

A) 

B) 

C) 

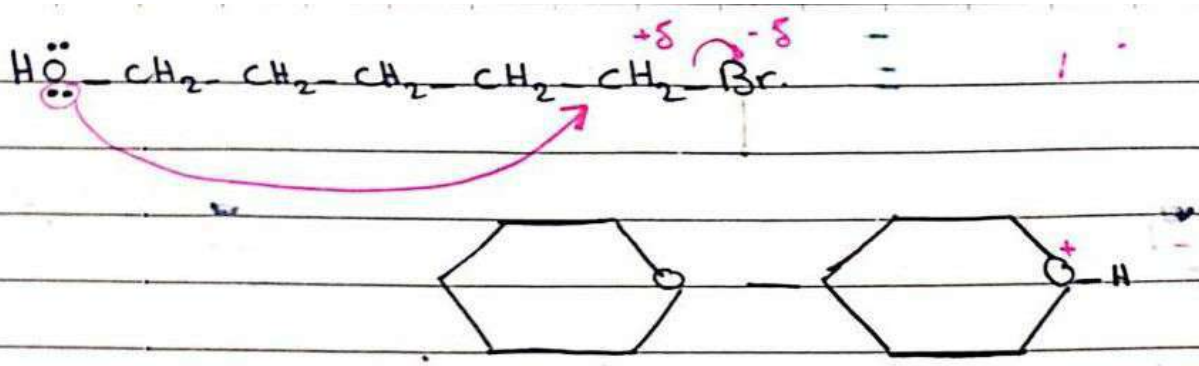
d) 

e) a + C.

- A accure Because it's benzyllic halide, C accure because it's 3° alkylhalide.
But B, d don't accure. so the answer is a+c.

- write Five difference between SN^1, SN^2.

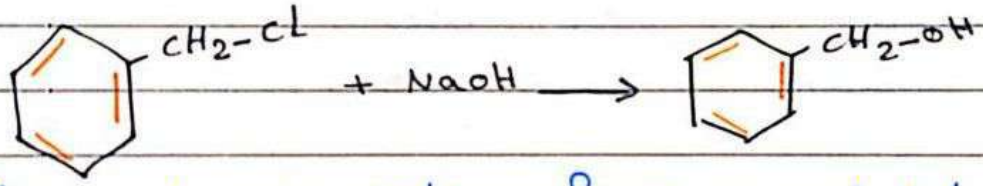
SN^1	SN^2
1- Unimolecular N.S	- Bimolecular N.S
2- occure in 3°, allylic and benzyllic halides	- occure in 1°, 2° halides.
3- generate acarbocation intermediate + halide ion	- generate intermediate [Transition state incoming nucleophile and outgoing halide ion].
4- yield 50% inversion and 50% retention "optical inactive"	- yield 100% inversion. "optical activity".
5- sp^2 hyberidization planer trangual	- sp^3 Tetrahedral.



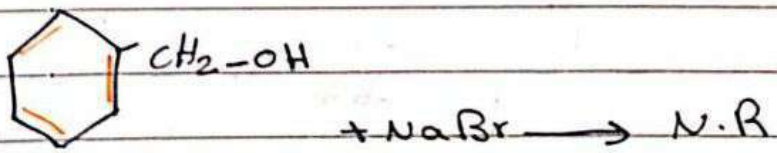
Notes

- A main condition for the occurance of the nucleophyllic substitution that the incoming is stronger than outgoing in basisty.

الشرط الرئيسي أن تكون المجموعة الداخلة أقوى من الخارجة



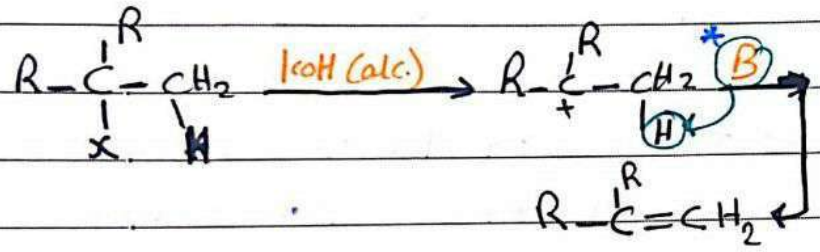
- Cl^- is weak conjugated base for strong acid HCl But OH is strong base. ;so it takes Cl's Place.



- Because the basisty of OH is two strong than Br.

S_N1 → E^1 : -3° -benzylic -allylic.

S_N2 → E^2 : -1°, 2°

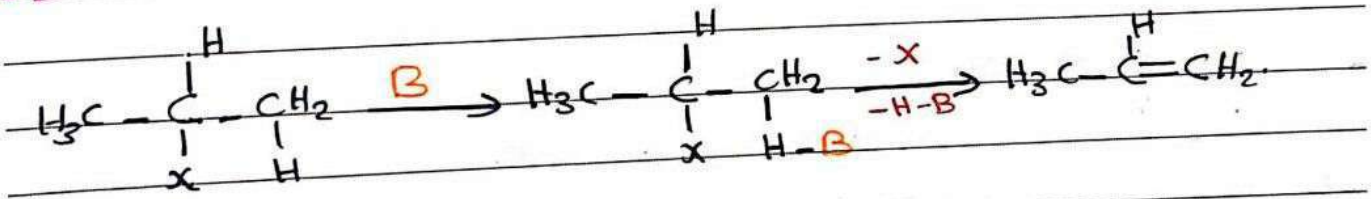


-Notes-

The Base take H from the carbon that is near carbocation, if there isn't Hydrogen the elemination don't occure.

- C-X bond breaks first to give a carbocation intermediate, followed by base removal of aproton to yield the alkene.

- E^2

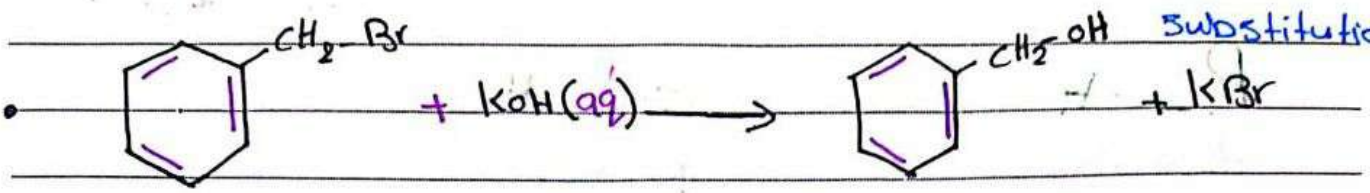


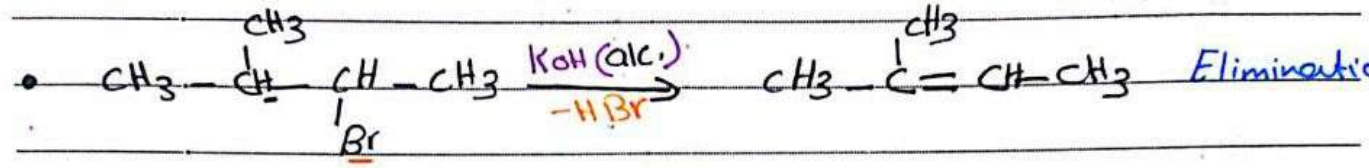
- C-H and C-X bonds break together (simultaneously), giving the alkene in a single step without intermediates.

Note :-

KOH (alc) → Elimination.

KOH (aq) → Substitution.



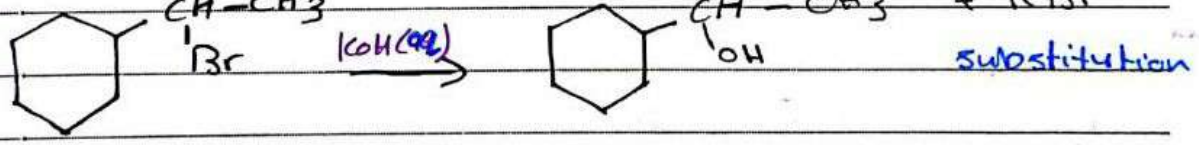


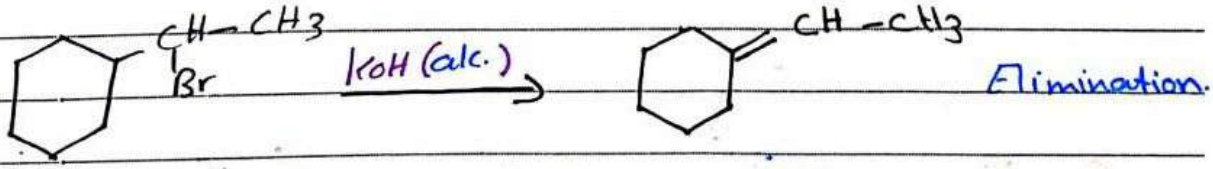
"Zaitsev Rule"

- formulated in 1875 by the Russian chemist Alexander Zaitsev.
- base induced elimination reaction generally (although not always) give the more stable alkene product, that is the alkene with more alkyl substituents on the double bonded carbons.

* The process of elimination will occure from left or right??
- sure it will occure from the left cause it has more alkyl substituents. due to Zaitsev Rule.

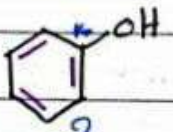
ex)

1) 

2) 

Alcohol

25/4/2020. Sat.
17th ele. lec.

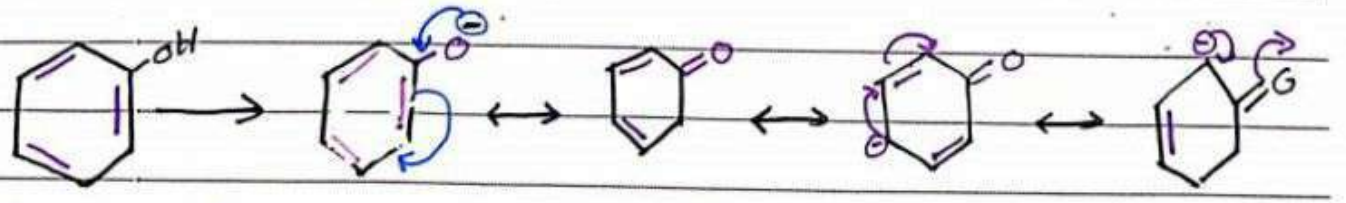
R–OH	Ar–OH
Alcohol	Phenol
CH_3OH	
sp^3	sp^2

- physical properties of alcohols :

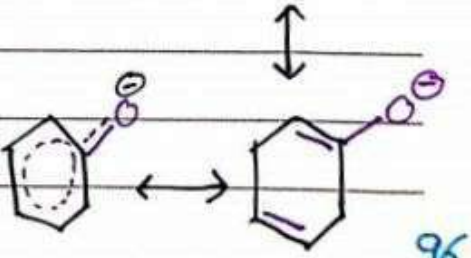
1. Soluble in water
   - $C_1 - C_5$ dissolve in water
   - ≥ not dissolve in water.

2. Boiling point B.p.
   alcohole ≫ alkanes. , Due to Hydrogen bond H.B

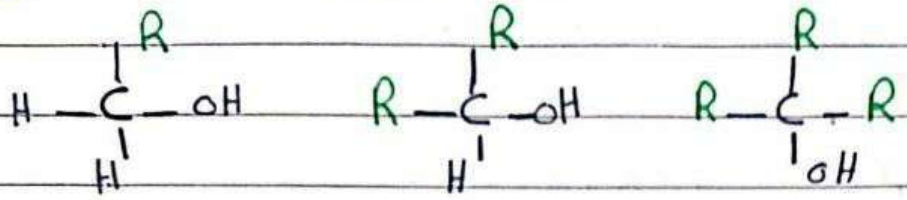
3. Acidity.
   - $R-OH \longrightarrow RO^- + H^+$
     weak acid. → strong conjugated base
   - $Ar-OH \longrightarrow Ar-O^- + H^+$



- Aromatic alcohol is more acidity than aliphatic Because of resonance.



• Types of alcohols :-

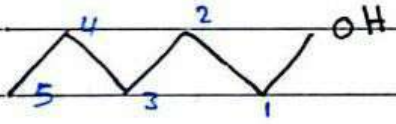


1° alcohol 2° alcohol 3° alcohol.

* which is more acidity ? .. 1°

• Nomenclature of alcohole.

1- Find the longest chain included the OH

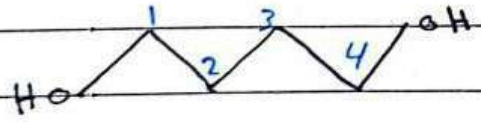


alkane → alkanole

pentanole.

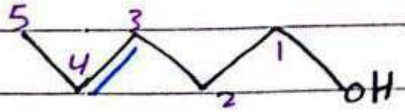
- If there is more than OH in the compound.

2: dioles, 3: trioles, 4: tetraoles.



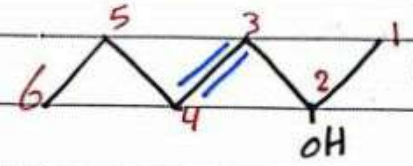
1,4 butandioles or
butan 1,4 dioles.

2- If the compound contain both OH and double bond the priority is for OH. and named enole



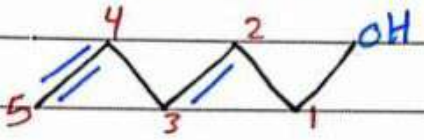
pent-3-enole or
3-pentenole.

3. Also If the compound contain triple bond the priority is for oH and we named yneole or ynole



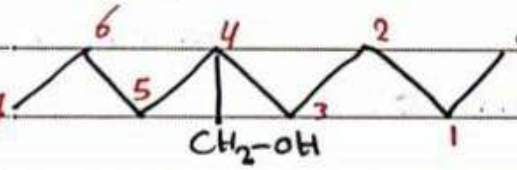
hex-3-yn-2-ole

4. If there is double, triple and oH we named enynole.

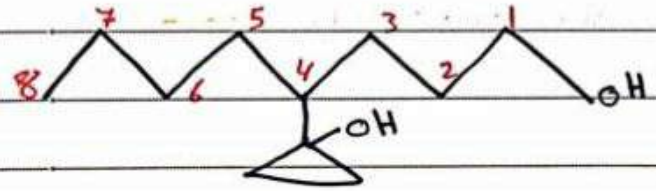


pent-2-en-4-ynole

5. If the oH present as substituted named hydroxy.

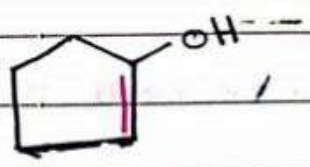


4(hydroxymethyl) heptanole.

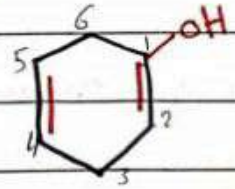


4(hydroxy cyclo propyl) octanole.

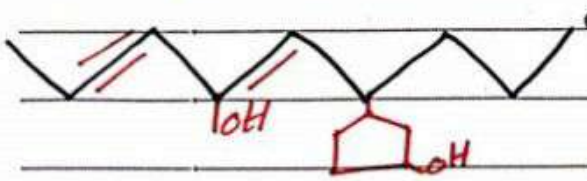
• Name the following compound:-



cyclo pentenole.



cyclo 1,4 dienole



3-(3' hydroxy cyclopentylole) oct-4-en-5-yn-1,5 dioles.

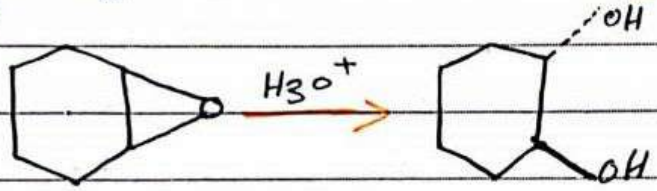
1- Hydrolysis of alkenes

2- oxymercuration - demercuration reaction also in alkenes

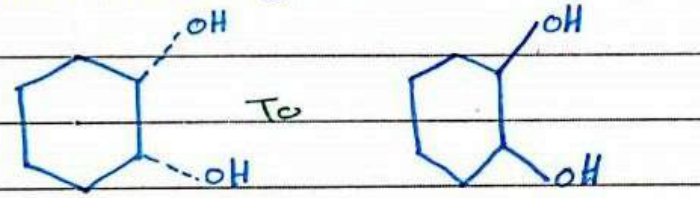
3- Hydroboration oxidation reaction alkenes

4- oxidation of alkene by cold ($KMnO_4$, OSO_4, $HCOOOH$) alkenes

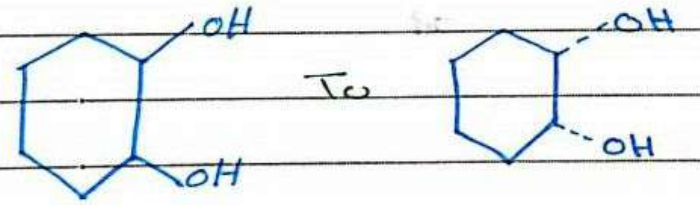
5- Hydrolysis of epoxide "Antihydroxylation"



- conversion of~



Question.



6- Reduction of carbonyl group.

Nucleophyllic center $\rightarrow -\delta \rightarrow$ electrophyllic addition

$+\delta \rightarrow$ Nuclophyllic addition

electrophyllic center

Note:-

- Depending on the additive we named the reaction

حسب الاداة المضافة نسمي التفاعل

- في reduction نضيف H^- والتفاعل Nuclophyllic addition.

• Reducing agent used for reduction:-

• $NaBH_4$: sodium borohydride , Selective R.A

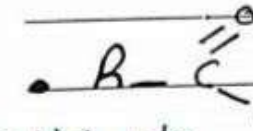
• $LiALH_4$: Lithium aluminum hydride., non selective R.A

• what is the difference between selective and non selective?

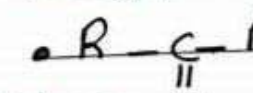
- selective reducing agent make the reduction just for Aldeyde and ketone  and 

But non selective reducing agent make the reduction for all function group that contain carbonyl group.

like:(Ester, carboxylic acid, ketone, aldehyde ----).

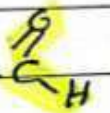
•  $\xrightarrow{R.A}$ 1° alcohol

aldehyde.

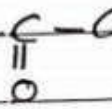
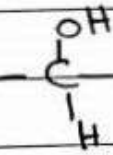
•  $\xrightarrow{R.A}$ 2° alcohol.

ketone

• Note: we keep number of carbon.

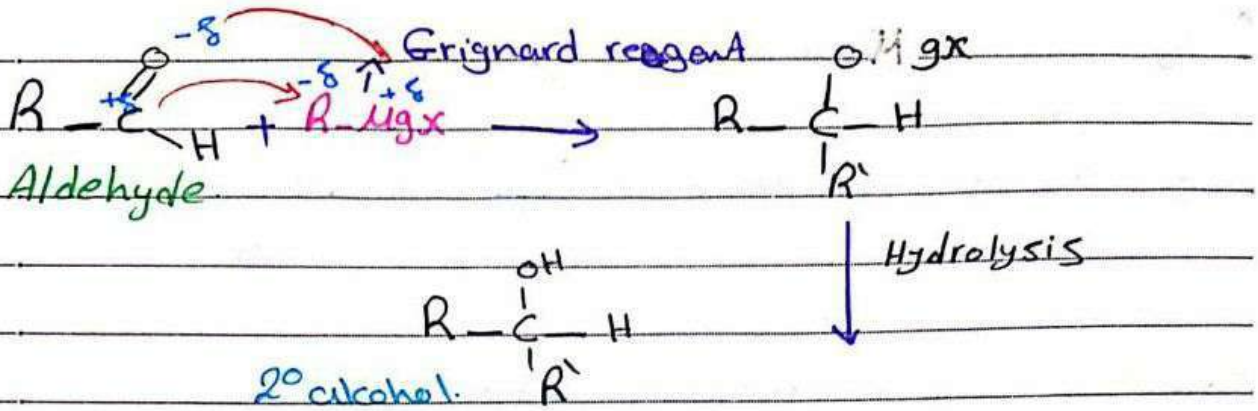
• CH_3-CH_2-  $\xrightarrow{NaBH_4}$ $CH_3-CH_2-CH_2OH$

aldehyde 1° alcohol.

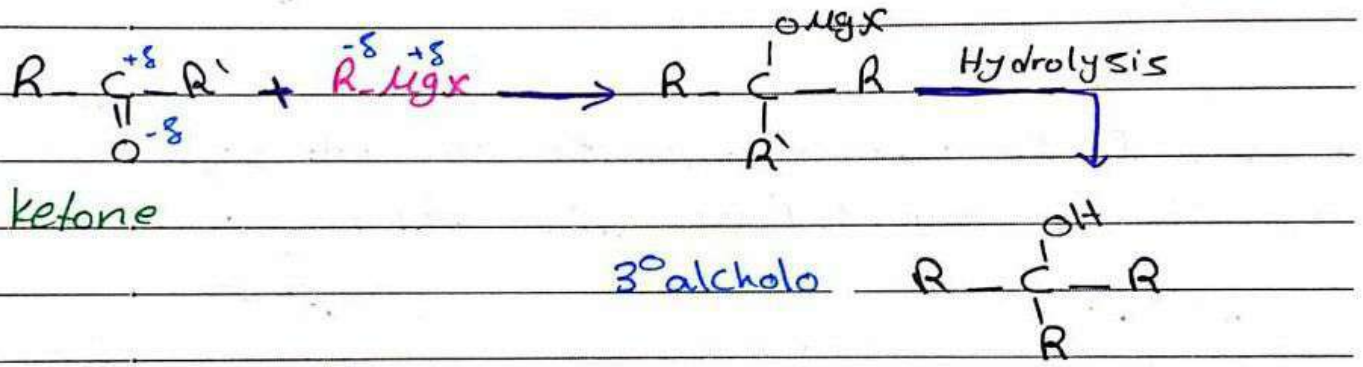
• CH_3-  $-CH_3$ $\xrightarrow{LiAlH_4}$ CH_3-  $-CH_3$

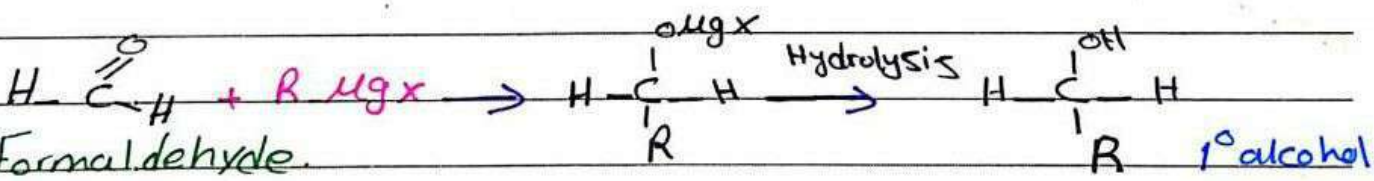
ketone 2° alcohol.

• While



If I want to yield 3° alcohol we use ketone insted of aldehyde.





Summary :-

• Formaldehyde + R-Mgx → 1° alcohol

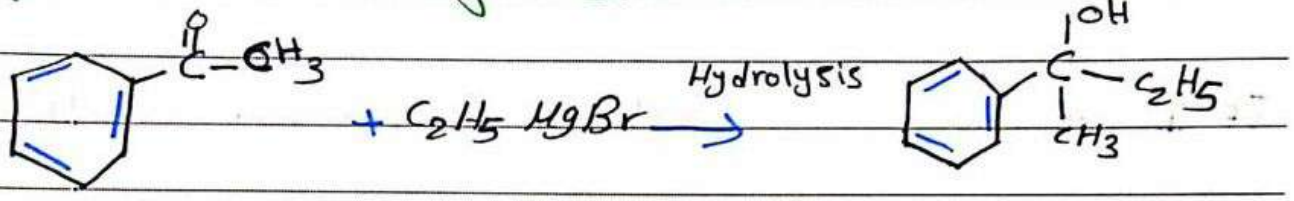
• Aldehyde + R-Mgx → 2° alcohol

• ketone + R-Mgx → 3° alcohol

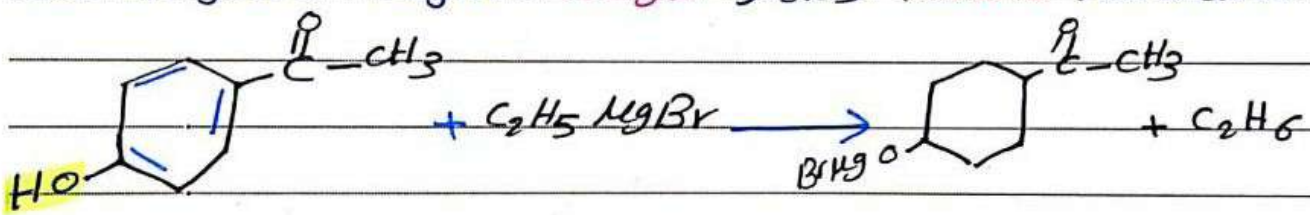
*

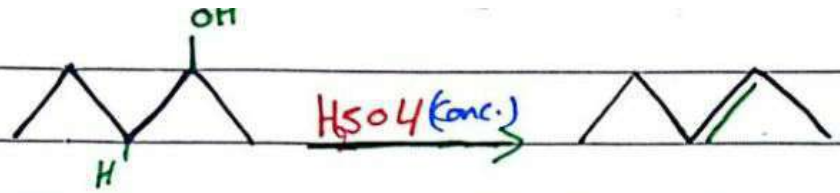
- $CH_3-CH_2-OH + CH_3MgBr \longrightarrow CH_4$ alkane.
- $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3MgBr \xrightarrow{\text{hydrolysis}} CH_3-\overset{OH}{\overset{|}{C}}(CH_3)-CH_3$ 3° alcohol

Complete the following reaction:-



* Note :- If the compound contain (SH, OH, COOH, SO_3H) with carbonyl and add Grignard reagent. RMgX yields Alkane not alcohol.



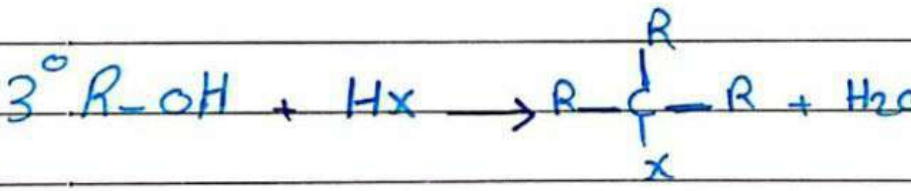


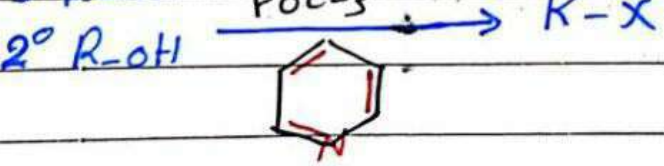
Note :-

- we can use .. H_2SO_4 , HCl , H_3PO_4 (conc.)
- we grab or remove Hydrogen from the group which has more alkyl group. "Zaitsev Rule".

في تحضير الكلوريدات

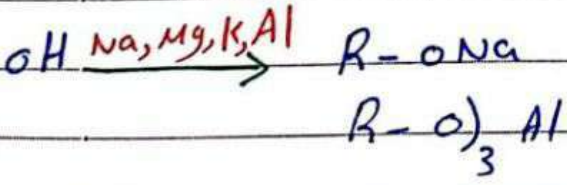
2-



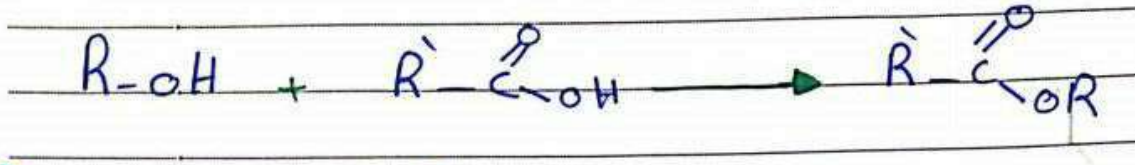


- we can use $POCl_3$, PBr_5 , PBr_3 , PCl_5 , PCl_3 .

3) with Active metal



4. with carboxylic acid C.A.



*** 5. oxidation of alchol

oxidizing agent

Mild

- MnO_4, CrO_3, PCC

Strong

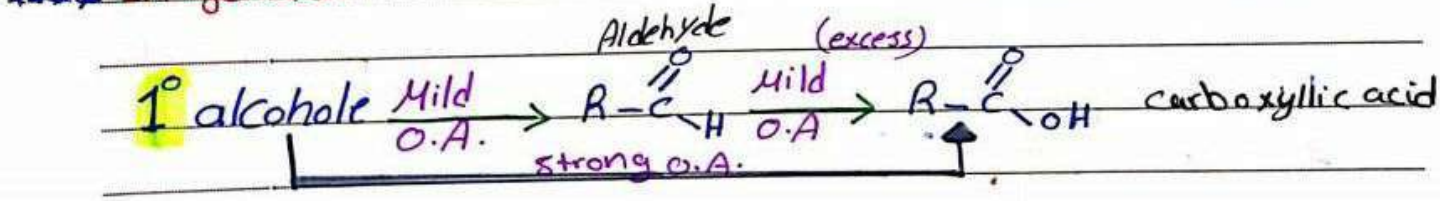
- $KMnO_4$, K_2CrO_7

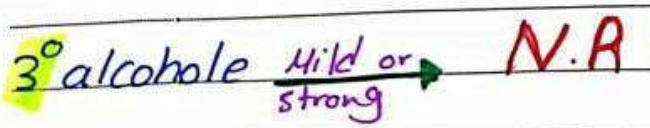
$[CrO_3 / H_2SO_4]$

↳ Jones reggent.

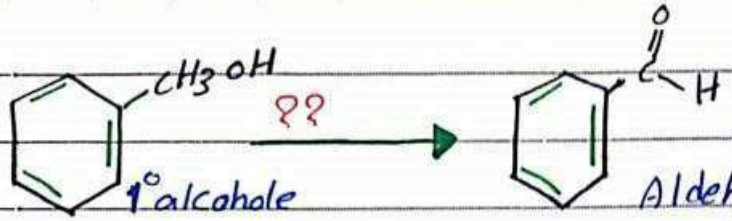
PCC: pyridinium chloro chromate

**** In general.

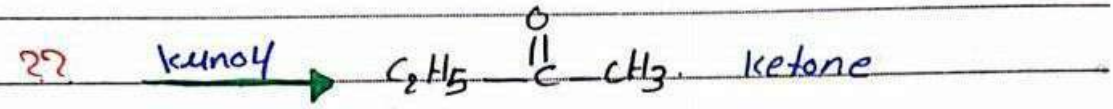


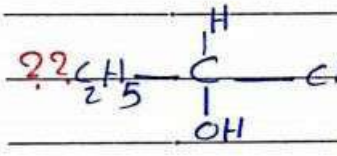


ex)



?? → PCC, CrO_3, MnO_2





Thiol RSH

* Thiole is analogs of alcoholes.

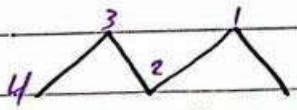
ROH RSH · which is more acidity ??

Thiol RSH Because O, S are in the same group and the acidity increase when we go from up to down ↓ O, S increasing of acidity.

• Nomen Clature of Thiol :-

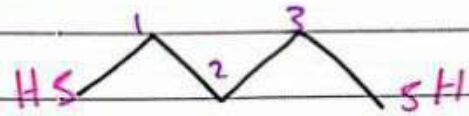
They are named by the same system used for alcohols with the suffix - thiol used in place of - ol

alkane → alkanthiol



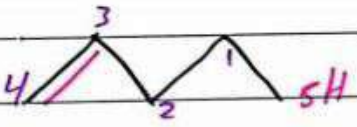
butanthiol

- If there is more than one thiol group in the compound
  2: dithiol
  3: Trithiol



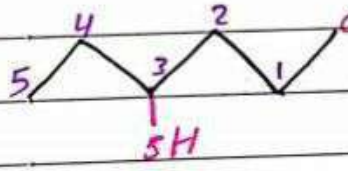
1,3 propandithiol

- If there's thiol group with double bond the priority for thiol group. or triple ≡



but-3-enthiol.

- If there's OH with SH the priority for OH and we named SH Mercapto as substituted.



3-mercaptopentanole.

Preparation of Thiols:

alkyl halide

1) $R-X + NH_2-\overset{\overset{:S:}{\|}}{C}-NH_2 \xrightarrow{NaOH} RSH$

Thiourea.

2) $R-X + \underset{\text{or } KSH}{NaSH} \longrightarrow RSH$

Reactions of Thiols:

1) oxidation of Thiols:

$$R\text{-}SH \xrightarrow{HNO_3} R\text{-}SO_3H$$

2.

$$R\text{-}SH + \underset{\text{or } KH}{NaOH} \longrightarrow \underset{\text{or } R\text{-}SK}{R\text{-}SNa}$$

$$\downarrow R\text{-}X$$

$$R\text{-}S\text{-}R$$

Thioether

Ether

3.5.2020, sunday
20th electronic lecture

R–O–R Ar–O–Ar

R'–O–R

Ar–O–R

In general Ether is a protic solvent

- Nomenclature of Common Name :-

- $CH_3-O-\overset{*}{C}H_3$ Dimethyl ether * symmetrical

- $C_2H_5-O-C_2H_5$ Diethyl ether or ethylether.

* A symmetrical :- → in this case we named according the alphabet.

- $CH_3-O-C_2H_5$

Methyl ethyl

ethyl Methyl ether.

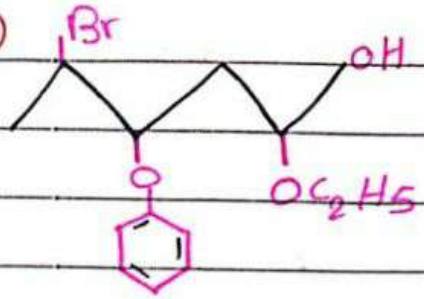
- Nomenclature of IUPAC :-

In IUPAC the ether is substituted

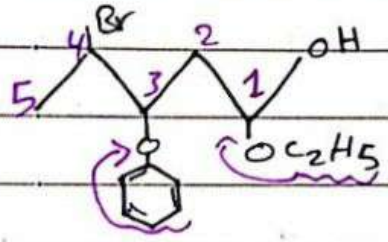
R–O → alkyloxy
alkoxy

Ar–O → phenyloxy
phenoxy.

ex) 1)

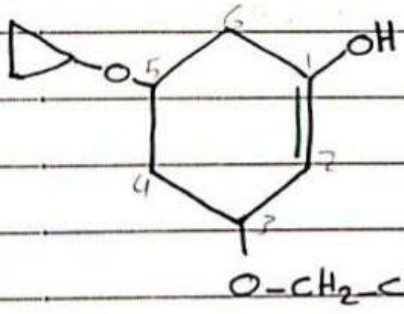


Sol.)



4-Bromo-3-phenoxy-1-ethoxy pentanole.

2)



5(cyclopropoxy)-3(Propoxy) cyclohexenole.

• Preparation of ether.

1) From alcohole.

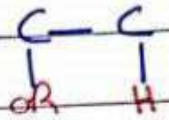
$$CH_3-CH_2-OH \xrightarrow[H_2SO_4]{\Delta} C_2H_5-O-C_2H_5$$

• The heat Δ has abig role in preparation of ether

$\Delta \leqslant 140 \rightarrow$ ether

$\Delta > 180 \rightarrow$ alkene.

2) Alkyloxy-mercuration demercuration reaction :-

$C=C + R-OH + Hg(CF_3CO_2)_2 \xrightarrow{NaBH_4}$ 

alkene alcohole

"Markovnikov"

↳ The Hydrogen gets attached to the carbon with more hydrogen substituents, and the oR gets attached to the carbon with more alkyl substituents.

- $(CF_3CO_2)_2Hg$ → mercuric trifluoroacetate.

ex)

$CH_3-CH=CH_2 + Hg(CF_3CO_2)_2 + C_2H_5OH \xrightarrow{NaBH_4}$

$CH_3-\underset{\underset{OC_2H_5}{|}}{CH}-CH_3$

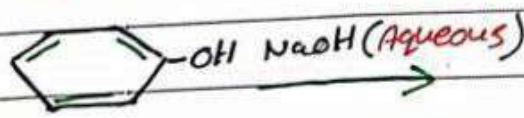
*** 3) Willimson Reaction :-

metalalkyloxide with 1° alkylhalide.

active metal تكون فعال

$R-X + \dot{R}-O-Na \longrightarrow R-O-\dot{R}$

1° alkyl halid



$R-X + \dot{R}-O-Na \longrightarrow R-O-R$

or $Ar-O-Na \longrightarrow Ar-O-R.$

• $CH_3-CH_2-Br + C_2H_5-ONa \rightarrow CH_3CH_2O-C_2H_5$

مثال قوي

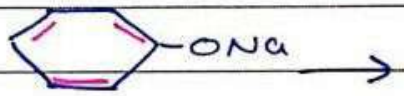
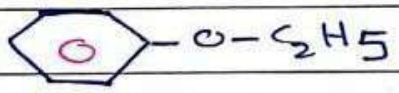
• $CH_3-CH_2-Br + H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-ONa \rightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3CH_2$

• $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + CH_3-CH_2-ONa \rightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

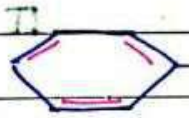
Strong Base

$3^\circ R-X$ "Elemenation"

T

• $CH_3-CH_2-Br +$  $\rightarrow$ 

T

•  $+ C_2H_5-O-Na \rightarrow N.R.$

Reactions of ether

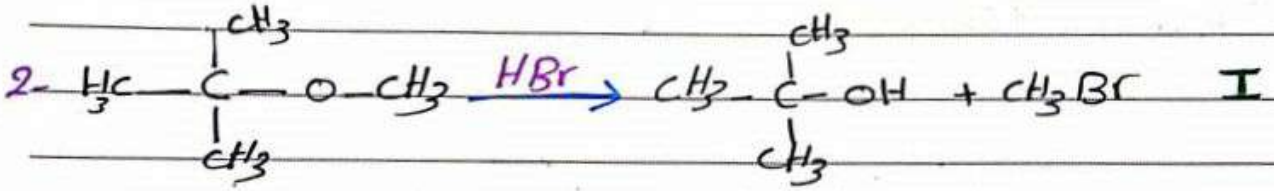
9/5/2020, Saturday
21st lecture
The last one.

Acid cleavage :-

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

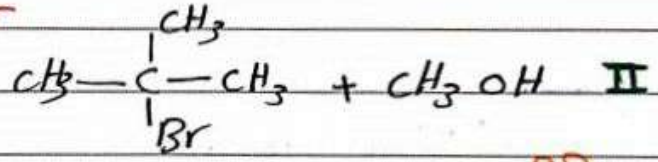
ex)

1- $CH_3-O-CH_3 \xrightarrow{HBr} CH_3OH + CH_3Br$

2- 

I

or



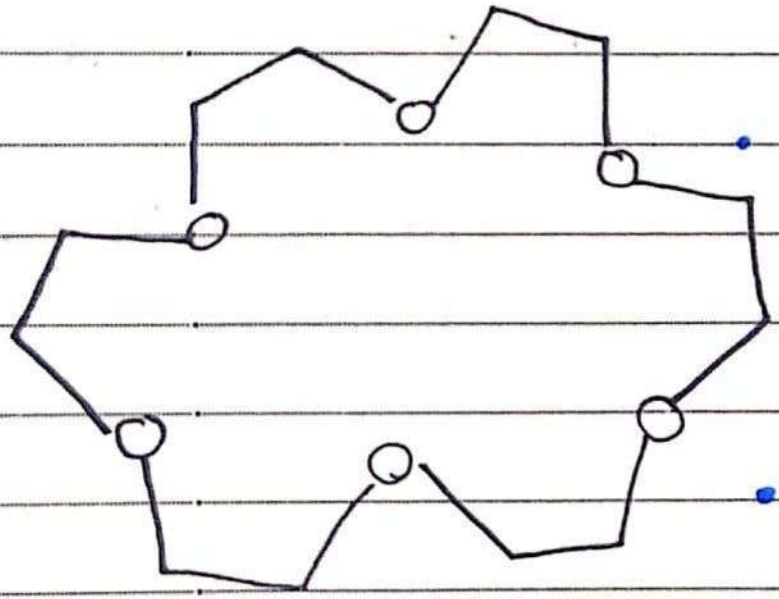
II

??

Tell why and give The explaintion :-

The answer is II

Identify the substitution pattern of the two group attached to oxygen in this case tertiary alkyl group and a primary alkyl group. Then, an ether with only primary and secondary alkyl groups usually undergoes cleavage by SN^2 attack of a nucleophile on the less hindered alkyl group, but an ether with a tertiary alkyl group usually undergoes cleavage by SN1 mechanism. In this case, an SN1 cleavage of the tertiary C-O bond will occur, giving 1 methanol and tertiary alkyl bromide.



• 18 crown 6.

• 12 crown 4

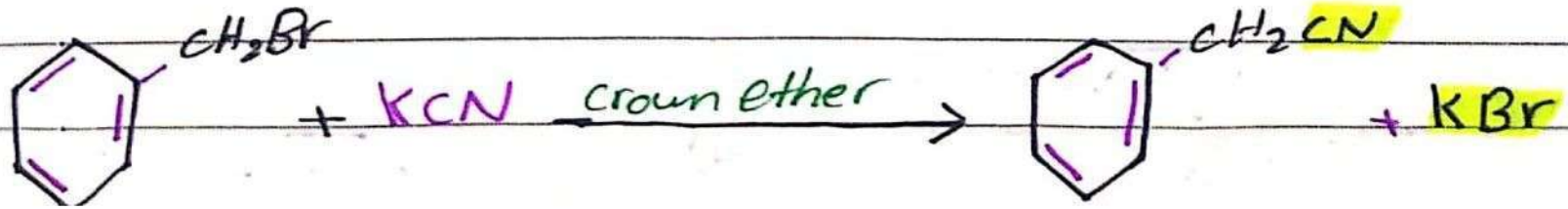
-Note:

- 18 is the number of total atom in the compound.
- 6 is the number of oxgen atom in the compound.

what is the point or benefit of croun ether ?

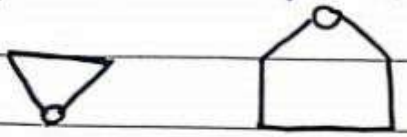
The importance of crown ethers is PTC

•PTC : Phase transf r catalyst.

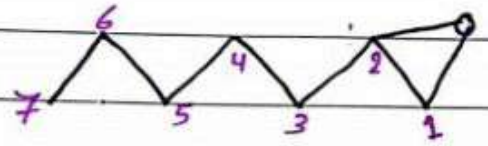


epoxide :-

The epoxide is cyclic Ethers.



- Nomenclature of epoxide :- epoxy.



1,2 epoxy heptane.

- we number the carbon atom which bonded with oxgen atom

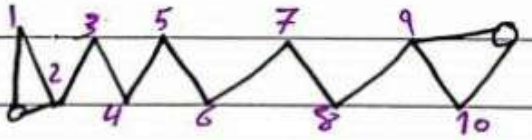
- نرقم ذرتي الكربون التي ترتبط بذرة الأكسجين.

- always the expoxide group is substituted.

- دائماً مجموعة epoxide تعامل معاملة ال قبل وبعد ثابت.

- If there is more than one epoxide group we named 2; diepoxy , 3; triepoxy _____.

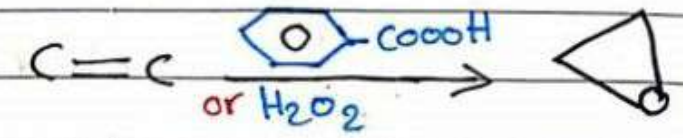
ex)

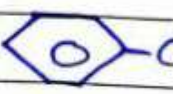


1,2g9,1o diepoxy decane.

- preparation of epoxide.

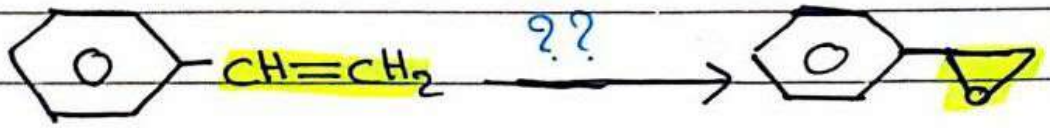
1. Halohydrine.
2. oxidation of alkene by peroxy benzoic Acid or H_2O_2.





peroxy benzoic Acid.

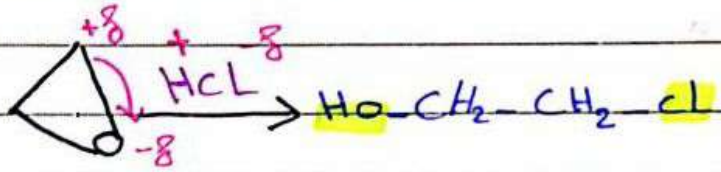
Complete the following reaction :-



?? → H_2O_2 or 

- Reactions of epoxide :-

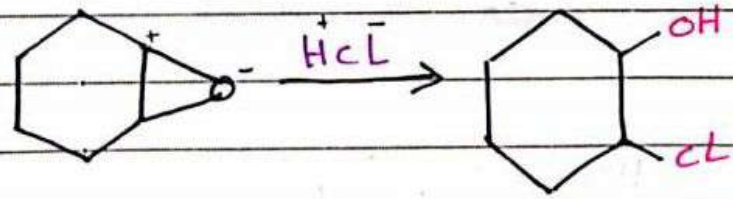
1) Acidic Hydrolysis.



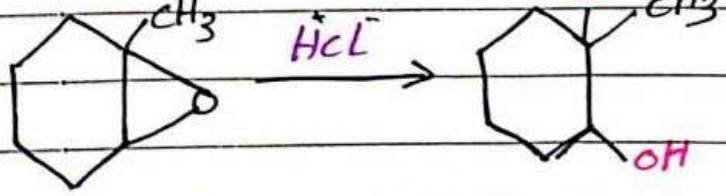
$\xrightarrow{H_3O^+}$ HO-CH_2-CH_2-OH

$\xrightarrow{C_2H_5OH}$ OH-CH_2-CH_2-C_2H_5

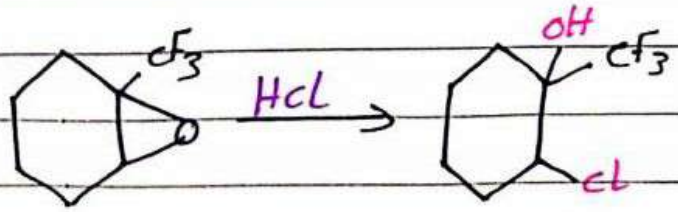
ex)

1-) 

ملاحظة تفرق لما يوجد مجموعة تؤثر على carbocation

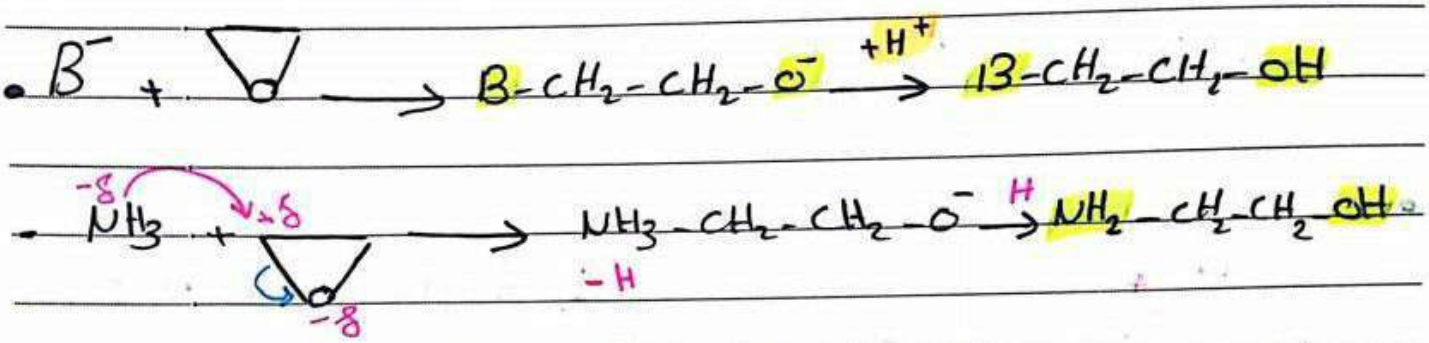
2) 

stability of carbocation.

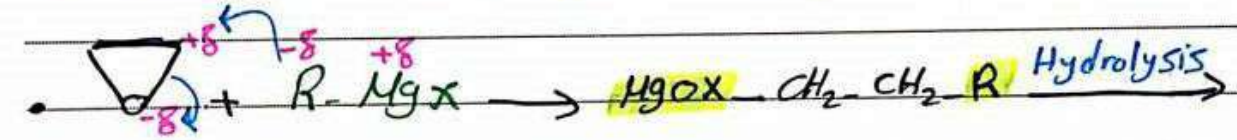
3) 

2-) Basic Hydrolysis.

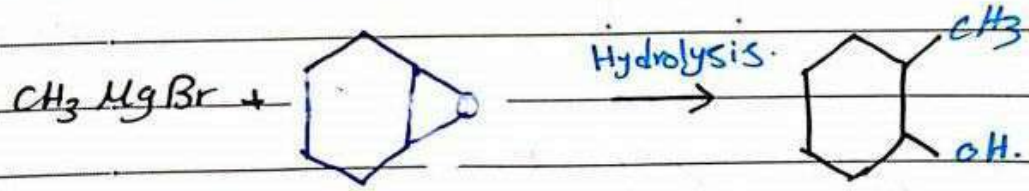
- Base in general B^- or $\ddot{B}$



3-) Reaction with Grignard Reagent.



ex)



Thioether = Sulfide.

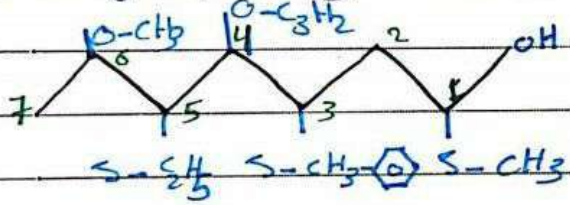
R–O–R R–S–R

Thiol Thioether.

• Nomenclature of thio ether.

CH_3-S-CH_3 : dimethyl (thio) ether.

• Thioether group always come as substituted.



or Propoxy
Propyloxy

1_methylthio or Mercapto_3_benzylthio_4_
5_ethylthio_6_methoxy heptane

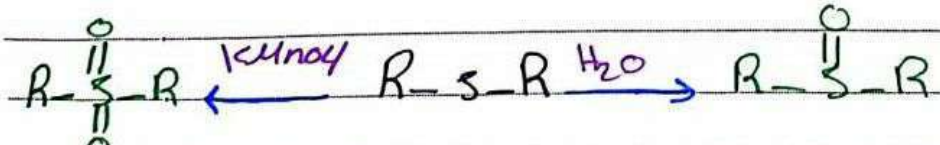
• preparation of thioether :-

thioether ينطبق عليه طرق تحضير ether ينطبق عليه طرق تحضير ولا

• Reactions of thioether :-

1- Acidic hydrolysis

2 oxidation of thio ether



sulfone sulfoxide.