Organic Chemistry

CH.1 → Bonding & isomorism

1.2 Ionic Bond : → * high melting points

Remeber that the ionic bond is between (cation & anion)

* dissolves into ions in water (soluble in water)

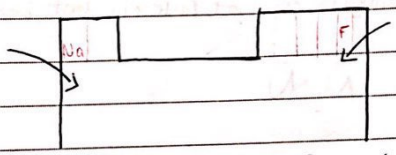
* Solids

electrostatic interaction between ions

(e.g.) NaF

$NaF \rightarrow Na^+ + F^-$

cation anion



occurs between them

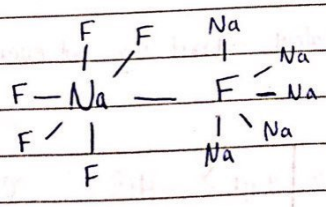
$Na: 1s^2\ 2s^2\ 2p^6\ 3s^1 \xrightarrow{-e^-} Na^+: 1s^2\ 2s^2\ 2p^6$

strong electropositive

$F_9: 1s^2\ 2s^2\ 2p^5 \xrightarrow{+e^-} F^{-1}: 1s^2\ 2s^2\ 2p^1$

strong electronegative

- ionic bond happens between strong electropositive & strong electronegative.
- ionic compounds are solid & have high melting points because of their arrangement in a lattice.



electropositive → tend to give up e^-

electronegative → tend to accept e^-

* بلورة من الروابط بين Na و F (كل وحدة حولها 6)

* سبب melting point al ionic compound عالي

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Covalent bond :

F - F * same electronegativity

F : $1s^2 / 2s^2\ 2p^5$ ★ لويس

↳ Valence electrons ① are responsible for bonding.

F_2 : $:\ddot{F}-\ddot{F}:$ * الرابطة الناتجة عن ال sharing اسمها covalent

sharing → * This sharing is even → pure covalent bond

(single bond)

O_2 : $:\ddot{O}=\ddot{O}:$ N_2 : $\ddot{N}\equiv\ddot{N}$

sharing sharing

(double bond) (triple bond)

* Bond Energy B.E N-N < N=N < N≡N

↳ minimum amount of energy required to break 1 mole of bonds.

* Bond lenght B.l N-N > N=N > N≡N

↳ distance between two nuclei at each end of the covalent bond.

1.5 Polar covalent Bond :

$HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ * as a molecule pure HCl is a gas.

more electronegative

$H-\ddot{Cl}:$ ⟹ its basically covalent → but its not even here

sharing

- Not a solid
- Not ionic
- although it forms ions in water

NaCl	HCl	Cl_2
ionic	Polar covalent bond	pure covalent

① Valence electrons
الإلكترونات التكافؤ

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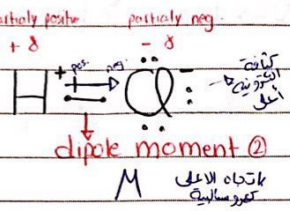
electronegativity : relative ability to attract covalent bond electrons.



* $\mu = 0 \rightarrow$ not apolar bond
* $\mu \neq 0 \rightarrow$ Polar bond
* P.C.B $\rightarrow$ تكون بسبب وجود فرق في الـ electronegativity

• electronegativity صفة للذرة

• Polarity صفة للرابطة

E.N increases →

C 2.6 N 3.0 O 3.5 F 4

S 2.6 Cl 3.1

Br 2.6

I 2.1

E.N increases

فرق في E.N

* Rank the following bonds according to their polarties :

1. C-O , C-F , C-N , C-C

C-F > C-O > C-N > C-C

2. C-Cl , C-F , C-Br , F_2 , C-I

C-F > C-Cl > C-Br > C-I > F_2

② dipole moment
عزم الاستقطاب

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[3] H-O , H-F , H-C , H-N , F_2

H-F > H-O > H-N > H-C > F_2

* مع عناصر نفس المجموعة ← كلما زادت E.N زاد الاستقطاب

1.7 Valence :

: Maximum # of bonds that an atom can make while Keeping the Charge Zero.

• يعتمد على عدد الـ e الذي تحتاجه الذرة لتطبيق الـ octet rule

	·C·	:S:	:O:	:F:	:Cl:	:Br:	:N	H·
Valence :	4	2	2	1	1	1	3	1

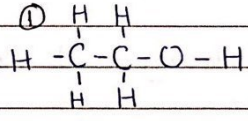
1.8 Isomorism :

[1] Moleculer Formula

[2] structural Formula

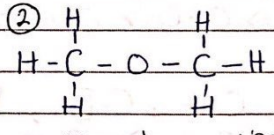
H_2O

C_2H_6 Two structural Formulas

① 

B.P 78°C

isomers

② 

B.P 23°C

* each structural formula represents a different compounds

* Isomers : are compounds with the same molecular formula but they have different structural formulas.

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1

• للحصول على المركب الثاني ← أكسر الرابطة ← أحرك ذرة / ذرات لمكان جديد ← أكون رابطة جديدة

Structural isomers (contitutional isomers)

* هناك عدة أنواع لـ isomers

* أكبر عدد ذرات H_2 يستوعبها المركب تساوي (عدد ذرات الكربون $2 + 2X$)

* أي نشاط يكون إمّا = أ و حلقة

C_3H_6

① open chain

② cyclic

① & ② are structural isomers

* أطول سلسلة كربون ← parent root

* Hetero atom → any atom that isn't H or C

C_6H_{14}

[1] * continous chain (No branches)

* $CH_3CH_2CH_2CH_2CH_2CH_3$ * condensed structure

* skeletal structure

Notes * any terminal / angle is C (Never shown)

* I dont show H unless its conneted to a hetero atom.

[2] First consititutional isomer → I remove first terminal Carbon & I connet it with the first internal Carbon. (أقل ال parent root)

substitution تفرع ← CH_3

$CH_3CH_2CH_2CHCH_3$

root

* branched

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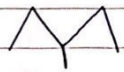
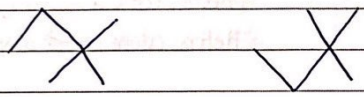
3 $CH_3-CH_2-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-CH_2-CH_3$



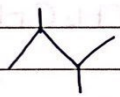
* branched

* $CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$] its identical with 2 Previous page

4 $H_3C-CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

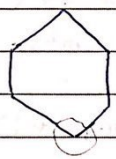


5 $CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$



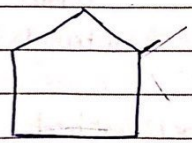
C_6H_{12}

1 cyclic



حلقة سداسية

2



حلقة خماسية

* pentagon & I add the carbon I removed as a substituant

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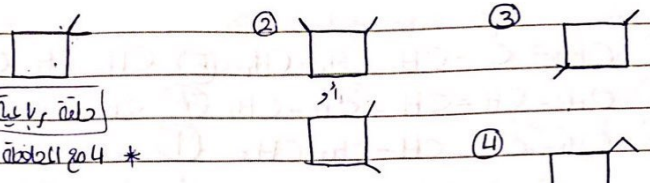
A- Cyclic → غير حلقي
open chain / double bond

③ ① ② ③



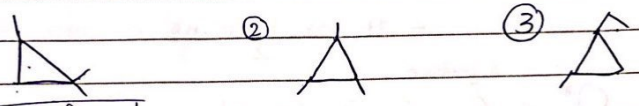
حلقة رباعية

أو

④

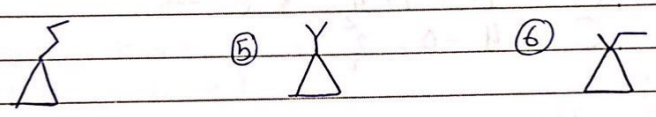
* 4 مع الحلقة على ال subs
* الكربون اللي طلعتي أضعها على أول sub ثم ابدأ فيها.

④ ① ② ③



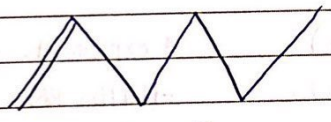
حلقة ثلاثية

④ ⑤ ⑥



* A-Cyclic

① $H_3C = CH - CH_2 - CH_2 - CH_2 - CH_3$



* على أحد كربونه ثم في اللي بكمل نقل ثم أغير مكان ال = ثم ال sub

② $CH_2 = CH_2\ CH(CH_3)\ CH_3$

③ $CH_2 = CH - CH(CH_3) - CH_2 - CH_3$

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④ $CH_2=C(CH_3)-CH_2-CH_2-CH_3$ ⑤ $CH_3-CH=CH-CH_2-CH_2-CH_3$

⑥ $CH_3-CH=CH-C(CH_3)H-CH_3$ ⑦ $CH_3-CH=C(CH_3)-CH_2-CH_3$

⑧ $CH_3-C(CH_3)=CH-CH_2-CH_3$ ⑨ $CH_3CH_2CH=CH-CH_2-CH_3$

1.11 Formal Charge :

$$= \#\text{ valence electron} - \#\text{ of non-bonding } e^- - \frac{\#\text{ of bonding } e}{2}$$

valence e^-

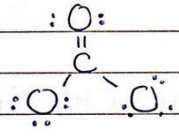
$$O^* = 6 - 6 - \frac{2}{2} = -1$$

$$O^{\Delta} = 6 - 4 - \frac{4}{2} = 0$$

$$C = 4 - 0 - \frac{2}{2} = 0$$

1.12 Resonance :

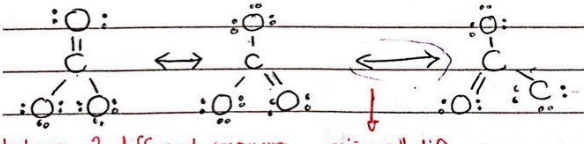
CO_3^{2-}



1 (C=O) 2 (C-O)

shorter with higher B.E

* experiments showed that :
- all the bond are the same B.E, B.L
- all O atoms have the same charge $= -\frac{2}{3}$



between 2 different resonance structures for the same compounds

هذا السهم يتغير

⇌ 2 different compounds in equilibrium.

* لا يوجد وحدة بينهم صحيحة ← كلهم مع بعض صحيح

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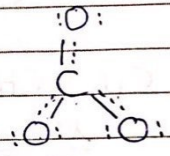
1

* Resonance → non-bonding e⁻ مع ال bonding e⁻ تبادل في ال
* electrons are not localized

① bonding → non
② non → bonding
③ both

• Resonance hybrid : the mix between all resonance structure

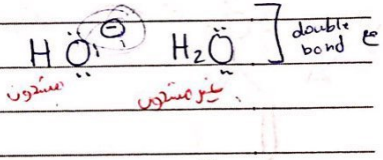
* The most correct structre
& the closest to reality



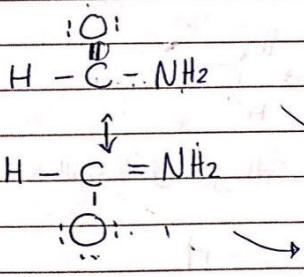
① $^{*}Z - Y \ddot{\ddot{X}} \longleftrightarrow Z = Y - X^{*}$

- The atom has :
  - * Charge (+ve or -ve)
  - أو * lone pair of electrons

neutral أو شحنة



Lone pair → مكان ال charge
charge ال → مكان ال lone pair

① 

* أنظر إلى الذرة التي عليها lone pair
ثم الذرة المجاورة لها حيث يجب أن
يكون عليها =

① $N = 5 - 2 - \frac{6}{2} = 0$
$O = 6 - 4 - \frac{4}{2} = 0$ } 0

② $N : 5 - 0 - \frac{8}{2} = +1$
$O : 6 - 6 - \frac{2}{2} = -1$ } C

* The Net Charge is the Same

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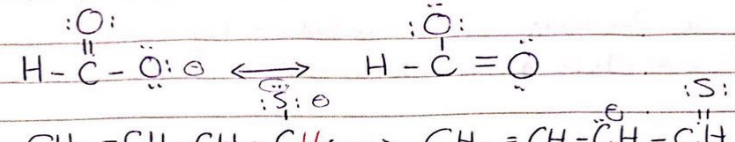
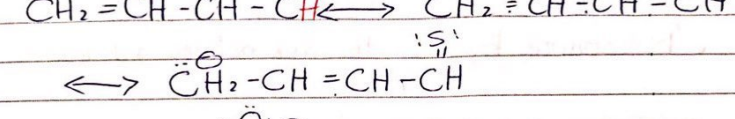
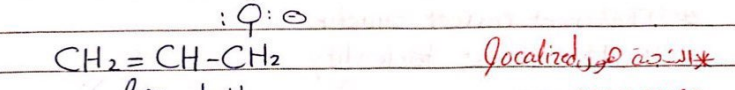




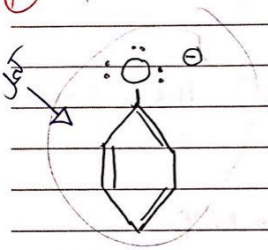


$CH_2 = CH - CH_2$

less stable

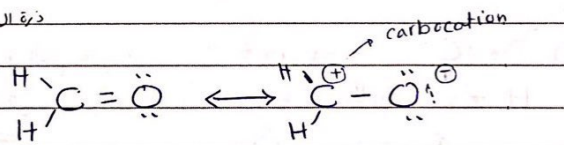
*النتيجة هو localized
no resonance

* الالكترونات أكثر ← كثافة الالكترونية أعلى ← تنافر ← تزداد طاقة الوضع
← نقل ال stability
بال resonance تتوزع الكثافة الالكترونية

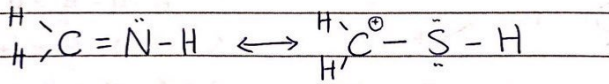


ذرة ال C.N هي اي من الذرة التي ارتبط بها أو بينها

2 ≡ أو =



* الذرة الأعلى كهروسالبية تسحب الـ e فتصبح سالبة والذرة الأخرى موجبة.



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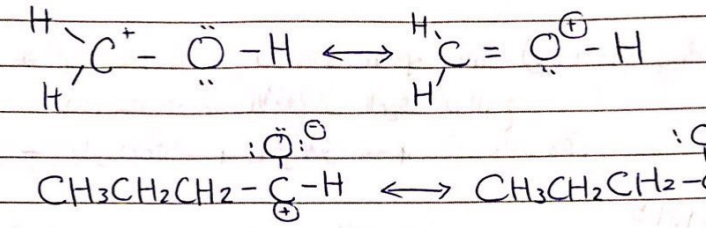
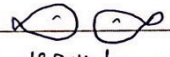
③ an atom with lone pair of e^- next to an atom with a positive charge.



1.14 V.B.T :

F-F $F: 1s^2\ 2s^2\ 2p^5$ ↑↓ ↑↓ ↑



half fillid half fillid overlapping

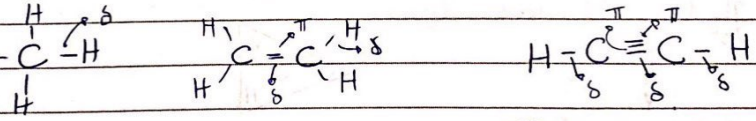
*البعيدة تتقلص ، القريبة تتقلص

*Only half filled Orbitals can overlap

* head to head σ

أي 2 يشكلو σ و π

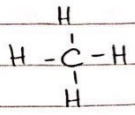
* side to side π



وحدة σ والباقي π

* في الـhybridazition صفات الناتج من نفس الصفات الأصل

↑↓ ↑↓ ↑ ↑ ↑



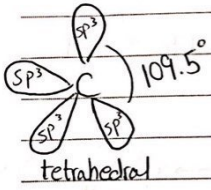
لازم يكون في تهجين حتى ينتج 4 افلاك ← 4 افلاك نصف ممتلئة ← 4 σ

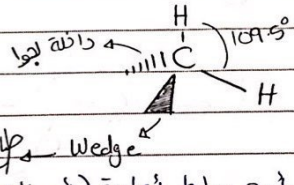
نصف ممتلئة.

* sp^3 شكله مثل P ولكن more spherical (يزيد اتجاهه بقيمة الربع)

لان فيه S من الأفلاك المهجنة هو الربع

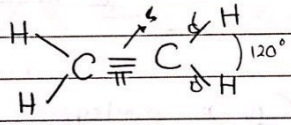
- يكبر حجمه ← تنافر أكثر ← يبتعدون عن بعض





* الكربونة المحاطة بأربع روابط أحادية (أو 4 مجموعات surrounding atoms / lone pair of e⁻) يكون تهجينها sp^3 وشكلها tetrahedral

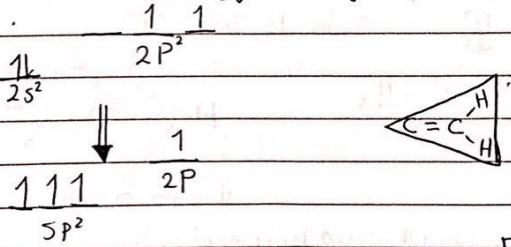
* أهم تهجين:



* 3 نصف ممتلئة ← 3 σ

* لازم يكون موجود P نصف ممتلئ ← 1π

* ذرة الكربون المحاطة بـ 3 σ و 1 π (أو عليها =) (أو حولها 3 مجموعات) تهجينها sp^2 / شكلها trigonal planar ، الزوايا بينها 120°



Groups	2	3	4
hyb	sp	sp^2	sp^3

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$H-C \equiv C-H$ (π π, 180°; σ σ) linear

- $2\pi \longrightarrow 2\ p$ orbitals

$\underset{2s^2}{\uparrow\downarrow}$ $\underset{2p^2}{\uparrow\ \uparrow}$ $\longrightarrow$ $\underset{sp}{\uparrow}\ \underset{sp}{\uparrow}$ $\underset{2p}{\uparrow}\ \underset{2p}{\uparrow}$ 2π

- SP $\longrightarrow$ more spherical

* يزيد بقيمة النص لأن نصفه S ونصفه P

* لما يكون حول ذرة الكربون (≡) أو مجموعتين: التهجين SP

linear الشكل

180° الزاوية

$\underset{sp}{1}$

CH.2 → Alkanes & Cycloalkanes ...

2.1 Alkane: hydrocarbonic (C & H only) compounds, all the bonds are single bonds.

* Here Carbons have the ultimate # of H atoms.
* Molecular formula C_nH_{2n+2}
* Hydrocarbons that → all the bonds are single
  → name ends with "ane"

التسمية: المجموعة الوظيفية - عدد ذرات الكربون

Formula	structure	name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_2$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	n-butane → مختلف تبعاً النهاية التفرع

لا يوجد تفرع

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$$H-\underset{\delta}{C}\equiv\underset{\delta}{C}-H \quad \text{linear}$$

$\pi\ \pi$ 180°

- $2\pi \longrightarrow 2\ p$ orbitals

$\underset{2s^2}{\uparrow\downarrow}$ $\quad \underset{2p^2}{\uparrow\ \uparrow} \longrightarrow \underset{sp}{\uparrow}\ \underset{sp}{\uparrow}$ $\quad \underset{2p}{\uparrow}\ \underset{2p}{\uparrow}$ 2π

- $sp \longrightarrow$ more spherical

* يزيد بقية النص لأن نصفه S ونصفه P

* لما تكون حول ذرة الكربون ($\equiv$) أو مجموعتين : التهجين sp

linear الشكل

180° الزاوية

$\underset{sp}{1}$

CH.2 → Alkanes & Cycloalkanes ...

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C_4H_{10}	$CH_3CH_2CH_2CH_3$	n-butane → عناصر تبدأ النهاية التفرع

لا يوجد تفرع

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Formula	Structure	name
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	n-pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	n-hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	n-heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	n-octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	n-nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	n-decane

2.3 IUPAC. Rules of naming of Alkanes:

* كل المركبات العضوية نفس الطريقة العامة مع اختلاف المقطع الأخير

$$CH_3-\underset{CH_3}{CH}-CH_2CH_2CH_3$$

1. look for the longest chain (root) containing the greatest # of carbon atoms → in alkanes we start & end with CH_3.
   * in this eg. → 2 longest chains that are identical & its pentane.

2. Identify the substituent (s): anything outside the root.
   أي sub يمين حسب عدد ذرات الكربون وينتهي بـ ال.

1. CH_3- methyl
2. CH_3CH_2- ethyl
3. $CH_3CH_2CH_2-$ propyl
4. $CH_3CH_2CH_2CH_2-$ butyl

* in this eg. → methyl → methylpentane الكلمة واحدة

* حسب الـ IUPAC لا يوجد أي فراغ بين الحروف :c

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2

n⊕n
L⊗L
n⊖L

3 Assign the position of the substituent (s) → the # of the carbon on the root → we select the least Possible # of the first sub.

* in this eg. 4 و 1 لما 2 اذن 2

$CH_3 - \overset{(1)}{\underset{(2)}{CH}} - CH_2CH_2CH_3$

* what separates # from letter is dash (-)

- eg. 2-methylpentane

مسبوق ال sub
2 - di
3 - tri
4 - tetra

- eg. $CH_3 - \overset{CH_3}{CH} - CH_2 \overset{CH_3}{CH} CH_2 CH_3$ → hexane

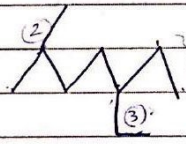
hexane
↓
methyl
↓
dimethyl hexane

ليست جزء من الاسم
هي فقط تعبر عن العدد

2,4 - dimethyl hexane

* comma is what separates # from #

- eg.



5
7
7
3

* according to writing the sub are written in alphabetical order (ethyl then methyl)

5 - ethyl - - methyheptane

* We take the least possible # for the first sub (we don't care about alph order)

5 - ethyl - 2 - methylheptane

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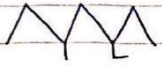
▫ eg.

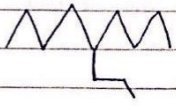


heptane → methyl / ethyl → 3 ← 3

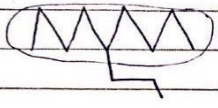
* لما يتساووا العدد الـ first sub ← يكون # least possible الـ alphabatical order

. 3-ethyl-5-methylheptane

▫ eg.



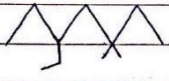
→ ارتباط في الـ terminal carbon



→ nonane

5-propylnonane

▫ eg.



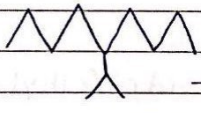
alpha order من عندنا ترتيب الـ dimethyl

5-ethyl-3,3-dimethylheptane

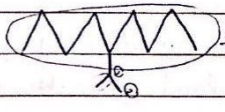
3	5,5	= 13
5	3,3	= 11

في مثل هذه الحالة
نأخذ المجموع

▫ eg.



→ ارتباط في الـ الوسطية



→ nonane

5-isopropylnonane

root

isopropyl

its a part of the name

CH_3 — CH — CH_3

root

$CH(CH_3)_2$

root

مركب في آخره ميثيل ومثيل مرتبطة بكربون في النص : iso

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* طريقة التسمية القديمة: الترقيم يبدأ من الذرة المرتبطة بالـ root حيث يكون رقمها "واحد"

1-methylethyl

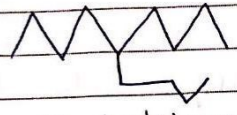
لا يختار آخر

5-(1-methylethyl) nonane

longest chain

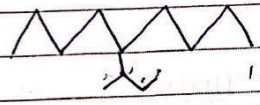
حطيناها هنا لأن الـ ethyl هي الـ root الـ sub نفسه

▫ eg.



5 - butylnonane

▫ eg.



1-methylpropyl

5- sec- butylnonane

butyl → terminal → butyl (الارتباط على)

butyl → internal → sec-butyl

ليست جزء من الاسم

لدى الكربونات المرتبطة بالكربون عدد 2

IUPAC name:

1-methylpropyl → sec-butyl

5-(1-methylpropyl)nonane

ضرورية

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* $CH_3\overset{*}{C}H_3$ primary Carbon — * الكربونة المرتبطة بكربونة 1 تسمى primary carbon 1°

* $CH_3-\underset{H}{\overset{H}{C}}_*-CH_3$ Secondary Carbon 2°

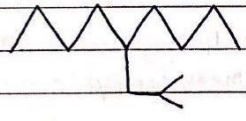
* $CH_3-\underset{CH_3}{\overset{H}{C}}_*-CH_3$ tertiary 3°

* $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ quarternary 4°

Sec-butyl | $CH_3-\underset{root}{C}H-CH_2CH_3$

dash يتبعهم

eg.



isobutyl

(2-methyl propyl)

5-isobutylnonane و 5-(2-methyl propyl) nonane

part of the name

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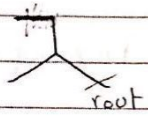
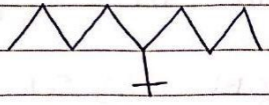


$CH_3-\underset{\underset{root}{|}}{CH}-CH_2$ (CH_3 above the CH)

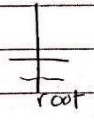
$(CH_3)_2\underset{\underset{root}{|}}{CH}-CH_2$

isobutyl

▫ eg.



5-tert-butylnonane أو 5-(1,1-dimethylethyl)nonane

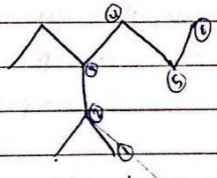


$CH_3-\underset{\underset{root}{|}}{C}-CH_3$ (CH_3 above the C)

$\underset{\underset{root}{|}}{C}(CH_3)$

tert-butyl

▫ eg.



* we have 2 longest chains & they are not identical. (3-ethyl-2-methylhexane)

*Halo alkanes : alkanes connected to a halogen. (Cl, Br, I, F)

* they don't have any priority in naming, we deal with them as normal sub(s)

choloro / floro / bromo / iodo

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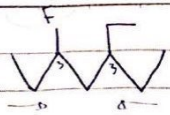
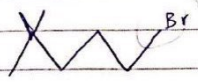
▫ eg.



3-ethyl-5-Fluroheptane

▫ eg.



1-bromo-4,4-dimethylpentane

2.7 Physical properties : ① BP ② Solubilty

* Alkanes have low B.P
* Alkanes are insoluble in water

* stronger intermolecular forces ⟶ higher B.P

molecule ⟷ molecule

↓ intermolecular forces

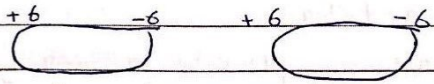
↓ in Alkane its Van der Walls

* Alkanes are insoluble in water because they are non-polar compound
* & like dissolves like

△E.N = 0.4 { C-H non-polar bonds
C-C non-polar bonds

* alkanes have low boiling points due to weak intermolecular forces (Van dar Walls).

* intermolecular forces arise from Partial Charges.



Van der Walls arises from ⟶ momentrly partial charges due to uneven disturbution of e^- [temprory dipole-dipole interactions due to uneven dis of e^-]

dis → distribution

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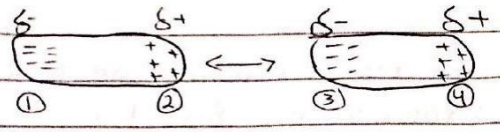


Boiling Point:

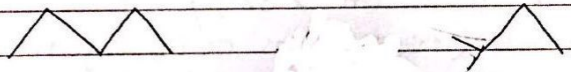
الفصل الثاني

[1] more carbon atoms → higher boiling points
(this applys to all organic compounds)

BP 36°C 63°C

* كلما زاد عدد ذرات الكربون ← زادت الكتلة المولية ← يزيد الوزن
← يحتاج طاقة أعلى حتى يفلت من السائل إلى الغاز

[2] more branching → less boiling point



n-pentane
B.P 36°C

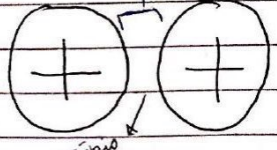
2-methylbutane
23°C

highly branched

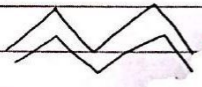
2,2-dimethyl propane
10°C

another name : neo-pentane

قريبين عن بعض اشي ما كرت ن
موعشان اشي (مريح)
فلازم بالي



منطقة تجاذب واحده



← continouse, unbranched

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* interaction sites in less branche are more (the more the branching the less the Surface area of interaction)

* المساحة أقل ← التجاذبات أقل

e.g. draw the Cons. isomer of ___ that has the lowest bp / highest bp

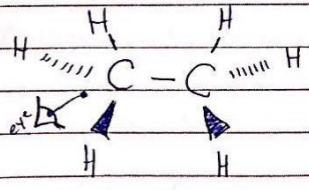
highly branched — cont. Chain

2.8 Conformation : isomers which are a result of the rotation of the C-C single bond about itself.

* We will have an infinte # of isomers but we will focus on 2 only :

① eclipsed (every atoms eclipsing the other atom)

* (الزاوية بين المستويين للذرتين يساوي صفر)



eclipsed.

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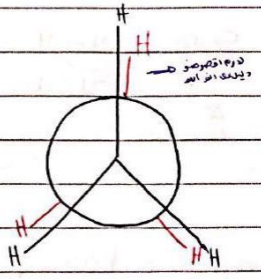
Newman projection :

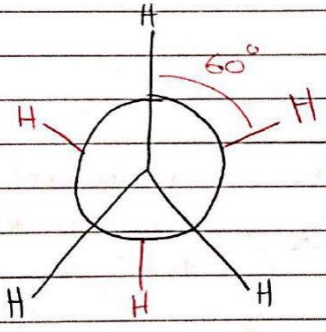
1) أحدد الرابطة التي يتم عليها "Confor"
2) أحدد الذرة من الرابطة

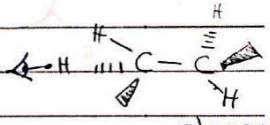
* في حالة الـ eclipesed نرسم بجانب كل خط أفقي خط قصير يمثل الروابط عن الذرة البعيدة عن العين (نحرف الـ eclipse 5° درجات حتى نرى الروابط)

* دائماً" نبدأ بالذرة القريبة ○
ثم روابط ثلاثة من قلبها ⊕



eclipsed
للاثيان ethane
(least stable)





staggered

Staggered
(most stable)

* eclipsed ⟶ least stable ⟶ لأن الذرات تكون أقرب ما يكون لبعضها مما ينتج repulsion.

* الطاقة المخزنة في الـ compound التي تكون أكثر من أقل طاقة سمي (trossional strain).

* its a result of repulsive interaction between bonding e. (eclipsed)

* it reaches it highest (Peek) in the eclipsed.

* كلما تدور عن الـ eclipsed يقل الـ strain (باتجاه staggered).

* الحالة الوحيدة التي يكون في الـ strain صفر هي staggered أي يكون trossional strain free

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Scanned with CamScanner

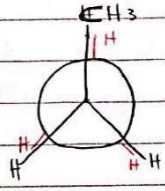
في الامتحان

* draw the possible conformation for ----→ use newman

Propane $CH_3-CH_2-CH_3$

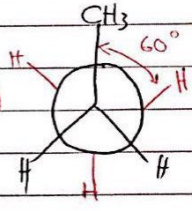
* the two bonds are the same between 1,2 / 2,3 (whatever you study you'll have the same conf)

eclipsed



* عند رسم الـ stag تبقى الأولية ودوري الـ الأولية

staggered



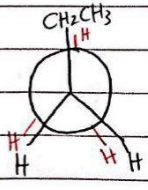
* propane has only 2 conf.

Butane $CH_3-CH_2-CH_2-CH_3$

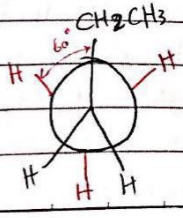
* three bonds
* 1,2 / 3,4 → terminal / identical → same conf → نسبة بار prob
* 2,3

(1,2 / 3,4)

eclipsed



staggered



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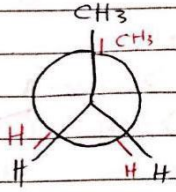
2

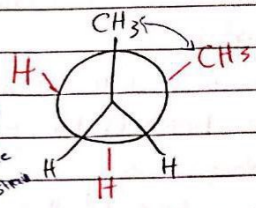
(2,3)

eclipsed (I)



strain { trosional
steric

staggered (I)

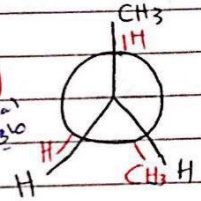


* trosional free
* steric strain

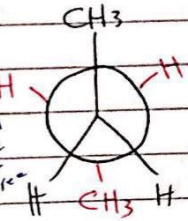
* المجموعات تتبع بعض Si
* المجموعات عكس بعض anti

eclipsed (II)

trosional
steric 3.6



anti-staggered



trosional free
steric free

strain free

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* Stability :

* The most stable one is :

anti-staggered > staggered I > eclipsed II > eclipsed I

staggered > eclipsed

no strain

due to ~~tor~~ strain

there is strain

eclipsed II > eclipsed I

* due to steric strain → its a result of the repulsion between the e^- of atoms

* كلما كبرت الذرة كبر حجمها ← يكبر المجال الذي يدور في التنافر فالتنافر أكبر ما يكون .

ec II > ec I

tor tor + steric

anti-st > st

no strain (strain free) steric

H.W

$CH_3-CH_2-\underset{I}{CH_2}$ $\underset{I}{CH_2}-\underset{I}{CH_2}$ $\underset{Br}{CH_2}-\underset{Br}{CH_2}$

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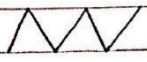
2.4 Cyclo-alkane :

* كل نقص في ذرتين H يجعل الالكانات الاصلية cyclic



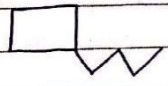
C_6H_{14}

C_6H_{12}

* التسمية: نفس الـ alkane بس نضيف Cyclo :

cyclopropane — cyclopentane — cyclobutane — cyclohexane

* الكربونة التي تكون جزء من الـ Cycle ولا علاقة لها بالـ Open

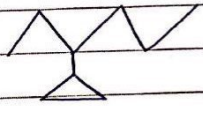


1-cyclobutylbutane

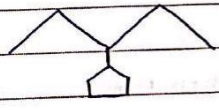
أو

butylcyclobutane

* اذا اعتبرت الـ cycle هو الـ sub لازم أعطي الرقم.
* إذا اعتبرت الـ cycle هو الـ root لا داعي لإعطاء الرقم.



3- cyclopropylhexane

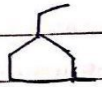


3-cyclopentyl pentane

* الأرجح أنه الـ cycle هو الـ sub
* إذا كانت الـ cycle على أي كربونة عدا الطرف نعتبرها sub
* إذا كانت الـ cycle على كربونة واحدة أختار بين الاثنين

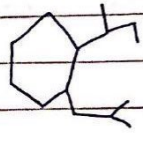
إذا كانوا نفس عدد الكربونات

* disubstituent :



1-ethyl-3-methylcyclopentane

* The earlier alpha order sub always has the # one.



1-sec-butyl-3-isobutylcycloheptane

ليست جزء من الاسم (b)

جزء من الاسم (i)

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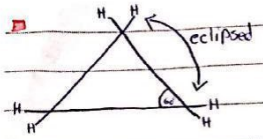
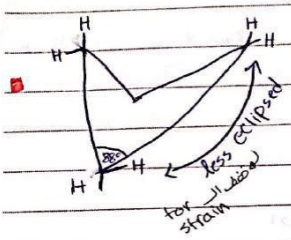
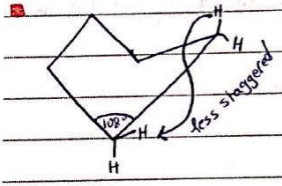


cyclopropane
(Planar) * all H_2 are perfectly eclipsed



cyclobutane
(Puckered) مثنى

*ذرتين مقابل بعضهم دائماً" إما فوق أو تحت



Cyclopentane
(Puckered)

* The type of strain in them is for (none of them is sta.)
* (ess st > (ess ec > ec (stability)
* △ < □ < ⬠ < ⬡

*الـ cycles أقل استقرار من الـ open chain ⇐ Propane > cyclopropane

* Cyclopropane ⟶ sp^3 التهجين ⟶ 109.5° الزاوية لازم تكون ⟶ 60° فعلياً

* The angle was squeezed to 60° & therefore energy was stored.
* angle strain: the energy stored as a result of squeezing the angle.

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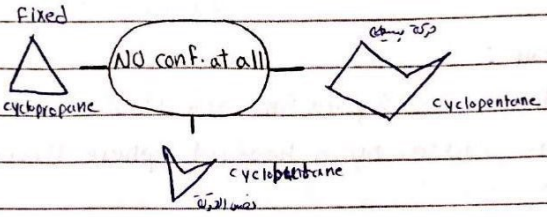
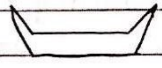


* Cyclopropane is the least stable due to (tor + angle) strain.
* cyclobutane ⟶ tor + angle (less than propane/more than pentane).
* Cyclopentane ⟶ little (tor + angle) (109.5 − 108)
* Cyclohexane ⟶ is the most stable, it is flexible because it has many conf.

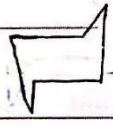
* Cyclohexane :

- I draw two lines parallel to each other one is shorter.

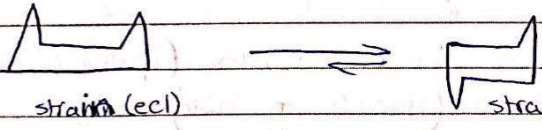


boat, suddle

- I draw two para lines one of them goes beyound the other



chair



* Chair is more stable & is the one present the majority of time 99.9%

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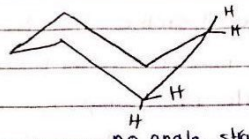
* Chair :

- drawn as 2 para lines مايلين / the two ends downward are close by a hedd of sphere facing forward العكس

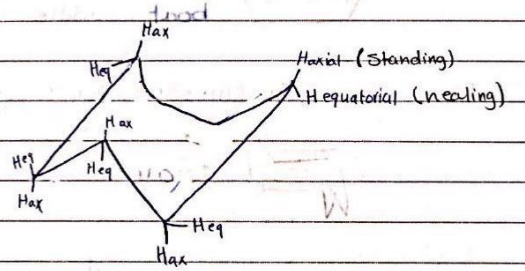


* كل الزوايا 109.5° ← no angle strain
* كل الروابط مع بعض ← stag. no tor strain

• مزايا هندسية :

* كل ذرة كربون اللي بعدها عكسها (down, up, down ....)
* كل 4 على نفس المستوى

* all hydrogens are perfectly standing eithe up or down



* the axial is with the carbon atom. (cup-H up / C down-H down)
* the equatorial is (oppsite + مائلة) → nealing

Perfectly standing

Carbon atoms :

3 up + 3 down

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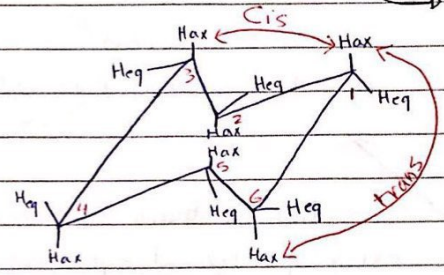
Problem 29 (cis / trans)

isomers → Constitutional
→ Stereoisomers → Conformers ناتج عن rotation من دون كسر
→ Configurational (cis + trans)



* Config isomers are found only in cyclic compounds & Alkanes (=)
* Cis / trans : is a concepts used to describe العلاقة الهندسية between 2 groups only.

trans ← * المجموعتين عكس الاتجاه — Cis ← * المجموعتين في نفس الاتجاه

* In alkanes → they rotate → cis turns to trans & trans turns to Cis
- that why we don't use cis / trans with them.

* $C_1 - C_2$ Hax - Hax trans
Heq - Heq trans
Heq - Hax Cis

* In $C_1 - C_2$, $C_1 - C_4$, $C_1 - C_6$ → المتشابهين : trans
المختلفين : Cis

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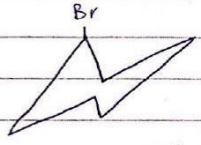
* In $C_1 - C_3$ Hax - Hax Cis
Heq - Heq Cis
Hax - Heq trans

* In $C_1 - C_3$, $C_1 - C_5$ → المتشابهين : Cis
المختلفين : trans

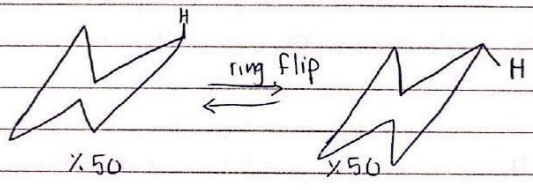
تذكر * Cis/trans تدخل في التسمية في ال disub



trans-1-Bromo-3-methylcyclohexane

* باقي ال cyclic ليس فيها eq و axi

* في ال Chair يتم تحول eq ⟵ ax والعكس بسبب rotation



nuclear magnetic reasonance : جهاز يستقر البروتونات ، يتعامل معها كمغناطيس لها مجال مغناطيسي يختلف عن Hax ⟶ Heq

* المفروض كل نوع له signal مختلفة لكن في الواقع أعطوا نفس ال signal

↓

لان الحركة سريعة جداً لم يستطع الجهاز التقاطها

↓

تمكن من التقاطها عندما خفضنا الحرارة إلى -90 .

↓

أعطوا 2 signals بنسبتهم لبعض %50 .

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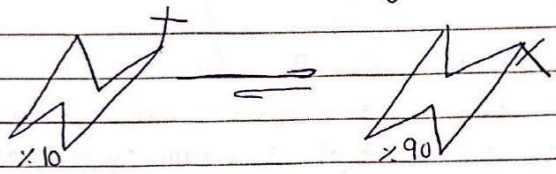
ring flip : Haxi → Heq
Heq → Haxi } → conformers نسميهم

* ينتج عن ال ring flip ← conformers

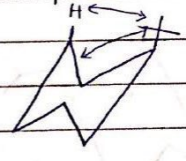


eq - tert-butyl
more stable

* ظهر ال Tert-butyl على ال room temp ← 2 conformers
* يوجد اتزان / يوجد ring flip ← لكن ال eq أكثر

* tert-butyl adopts eq position
* adopts → more stable → less repulsion
* here there is no ~~tor strain~~ , no ~~angle~~ strain
✓ steric strain

tert-butyl : is a bulky group → has steric strain
↓
interacts with ax hydrogens



* In mono-sub cyclohexane when a bulky group is in axi position it causes steric strain
* كلما كبرت المجموعة ← يزيد ste strain ← لذلك تعمل ring flip

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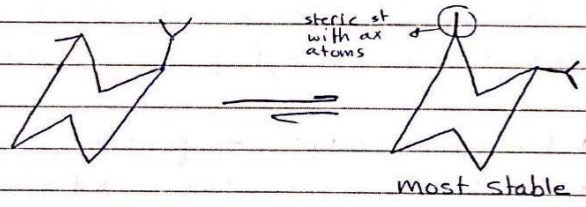
eg. draw the most stable → you draw the eq.
- ethyl - cyclohexane
- bromo - cyclohexane

* Disubstituted cyclohexane

draw the most stable conformation of

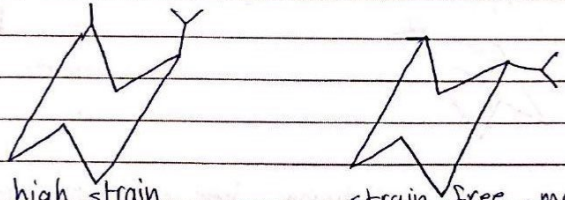
- trans - 1 - isopropyl - 3 - methylcyclohexane

2 sub → 2 conf (axi مرة ، eq مرة) (لا واحد مرة)



* المجموعة الاكبر في axil ← st strain أقل

- Cis - 1 - isopropyl - 3 - methyl cylohexane



high strain — strain free, more stable

* الـ rotation لا يغير بين Cis و trans

* Conformers → results from rotation
* Config → I break the bond & change the Oriention of one of the groups on the same C & creat a new bond.

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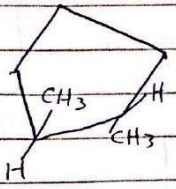
2

* Const isomers → I breaks bond & creat new ones on different location

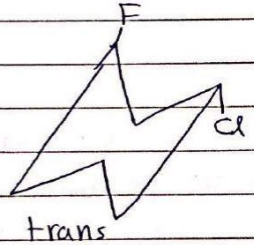


trans-1,2-Dimethyl cyclopentane

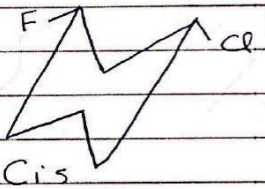
~~* trans 1,2 Dim~~

* cyclo propane / 4 / 5 → the shapes are fixed

axi / eq ci's / trans

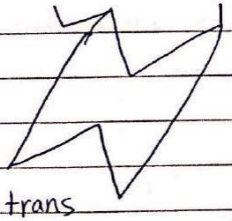


trans

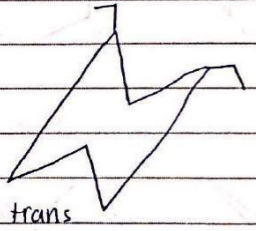


Cis

• cis - trans configurational isomers



trans



trans

conformers

axi ← eq ✓ *

eq ← axi ✓ *

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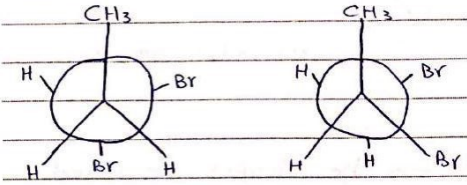
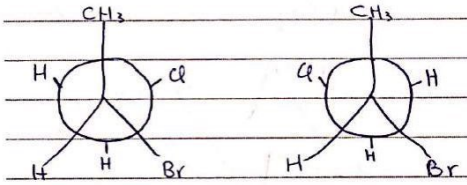
2.11 Isomerism:

* isomers
  - Constitutional
  - stereoisomers
    - conformers
    - Configurational (cis / trans)

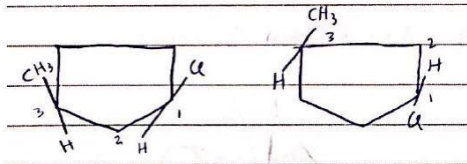


Const. isomers



Conformers

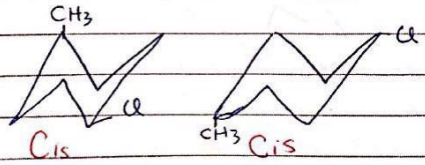
*أدير موقع مجموعتين 2 وأقارن



Cis - trans Conf. isomers

3,2,1 مع 3,2,1

Cis trans



Cis Cis

1,2,3,4 مع 1,2,3,4

Cis Cis ⟹ They are the Same

axil تقابل axil / eq تقابل eq

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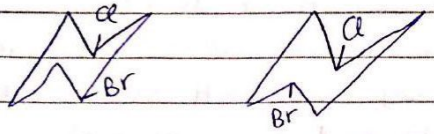
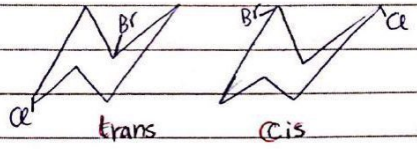
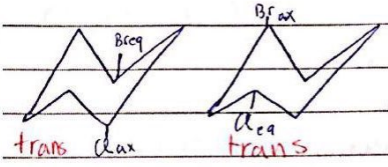


*نقل واحدة من الذرات من موقع إلى موقع آخر (const.)



Cis-trans conf. isomers



Conformers

*حدث ring-flip

2.12 reactions of alkanes

I) Oxidation (combustion)

*ذاتين لعدم وجود bond عاطم
inert

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

* When there is sufficient amout of O_2 the rxn gives CO_2.

* قد تكون المشكلة في عدم وجود كمية مناسبة من O_2 أو عدم حدوث خلط مناسب.

CH_3CO_2H
CHO_2H
$H_2C=O$
$C=O$
CH_3OH
C

هذا الناتج هو الذي يحدث

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*وجود O_2 بشكل كافي يؤكسد الـ C_2 أقصى ما يمكن ويكون له أكبر عدد تآكسر $O=C=O$

* كلما زاد عدد ذرات O_2 حول الكربون يزيد عدد التآكسر

* كلما زاد عدد ذرات H حول الكربون قل عدد التآكسر

* more O_2, less H, more double bonds, less single bond

Oxidation state :

اشوف O شحد أكتر = ما أنسحب لـ H

① $O=C=O$

② $CH_3-\overset{O}{\overset{\|}{C}}-OH$ ما بدو H

③ $H=\overset{O}{\overset{\|}{C}}-OH$ ما بدو H

④ $C=O$

⑤ $H_2C=O$

⑥ H_3C-OH

⑦ C

Oxidaton state increases

*أي ذرتين على طرفي الـ symmetry تشبه بعضها.

* أي ذرة على مستوى الـ sym تشبه نفسها فقط.

[2] halogenation

(Substitution عملية استبدال)

$$CH_4 + X_2 \xrightarrow[\text{heat}]{hr \rightarrow \text{light}} CH_3X + HX$$

$X_2 = Cl_2, Br_2, I_2$ (لا يعملها F_2)

$$CH_4 + Br_2 \xrightarrow{hr} CH_3Br + HBr$$

$$\xrightarrow[Hr]{Br_2} CH_2Br_2 + HBr$$

$$\xrightarrow[Hr]{Br_2} CHBr_3 + HBr$$

$$\xrightarrow[hr]{Br_2} CBr_4 + HBr$$

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* فعلياً لا يستخدم في التحضير ـــ لكن يستخدمه
* مشكلة هذا التفاعل أنه ليس فيه انتقائية حيث يستمر الـ Br_2 باستبدال الـ H وينتج mixture .
* يستعامل معه على أنه انتقائي ويبدل H واحدة.

halogenated

mono Chlorinated product

$$CH_3CH_3 \xrightarrow[Br_2]{hr} CH_3-\overset{Br}{\overset{|}{C}}H_2$$

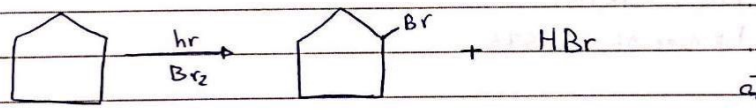
وزن يستخدم

$$CH_3-CH_2-CH_3 \xrightarrow[Cl_2]{hr} CH_3CH_2\overset{Cl}{\overset{|}{C}}H_2 + CH_3-\overset{Cl}{\overset{|}{C}}H-CH_3$$

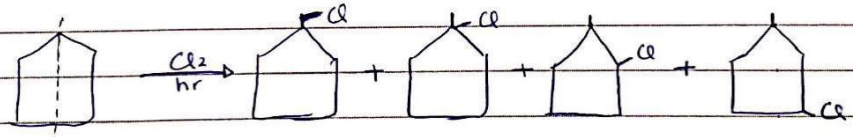
مختلفين

$$CH_3CH_2CH_2CH_3 \xrightarrow[Br_2]{hr} CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}H_2 + CH_3CH_2\overset{Br}{\overset{|}{C}}HCH_3$$

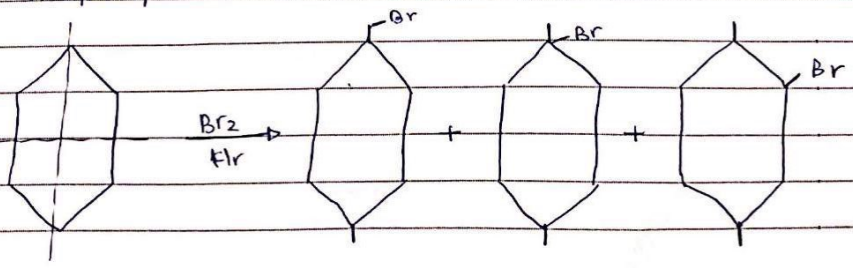
$$CH_3CH_2CH_2CH_2CH_3 \xrightarrow[hr]{Cl_2} CH_3CH_2CH_2CH_2\overset{Cl}{\overset{|}{C}}H_2 + CH_3CH_2CH_2\overset{Cl}{\overset{|}{C}}HCH_3 + CH_3CH_2\overset{Cl}{\overset{|}{C}}HCH_2CH_3$$



واحد فقط لأن كل الكربونات متشابهة



plain of symmetry



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2.13 Free radical chain mechanism:

$$CH_4 + Cl_2 \xrightarrow{hr} CH_3Cl + HCl$$

[1] Initiation: → happens on a small scale → كمية معينة قليلة من Cl_2 تتحول إلى free radical ثم يدخل فورا" في التفاعل.

← سهم بنصف رأس

$$Cl - Cl \xrightarrow{hr} Cl\cdot + Cl\cdot$$

* تكسر الرابطة وتروح تاخد الكترونها

free radical → uncoupled electron → wants coupling → very reactive

[2] Propagation: (Alkyl Free radical) * يهجم الهيدروجين على الالكان ويتفاعل مع الهيدروجين ويكون

$$Cl\cdot + H-CH_3 \longrightarrow \cdot CH_3 + H-Cl$$

Alkyl free radical

$$H_3C\cdot + Cl-Cl \longrightarrow H_3C-Cl + Cl\cdot$$

Alkyhalide

① Initiation:
neutral → free radical

② Propagation:
Free radical + neutral → Free radical + neutral
(H−X / alkyhalide) products انتاج ال [1] : propagation مهمة ال *
[2] يتم انتاج ال alkyl free radical لاستمرار التفاعل.

③ Termination:
free radicals → neutral

* مهمة ال initiation : انتاج كمية قليلة من ال free radicals لبدء التفاعل

[3] Termination:
① $CH_3\cdot + Cl \longrightarrow CH_3Cl$
② $Cl\cdot + Cl\cdot \longrightarrow Cl_2$
③ $CH_3\cdot + CH_3\cdot \longrightarrow CH_3CH_3$ (by product) منتج جانبي غير مرغوب
→ longer chain alkane

con. ⇒

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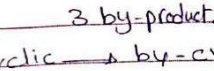
* مثلاً لو بدأنا بـ Propane ← 3 by-product

cyclic ← by-cyclo



• eg: write the propagation steps of _____

• eg: Which of the following is propa / init steps?

CH.3 AlKenes : C_nH_{2n}

كل double bond تمثل 2H

• $CH_2=\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=CH_2$ Conjugated

• $CH_3-\overset{H}{\overset{|}{C}}=C=\overset{H}{\overset{|}{C}}-CH_3$ Cumulated

• $CH_2=\overset{H}{\overset{|}{C}}-CH_2-\overset{H}{\overset{|}{C}}=CH_2$ non-conjugated (isolated)

* إذا = 1 ← كلهم نفس التصريف. * أكثر من = ← دالات.

① conjugated = — =

② أكثر من — تفصل بين 2 = isolated / non-conjugated:

③ Cumulated = = (? Alenels)

2 double bonds on one Carbon

3.2 Naming of AlKenes :

* We look for the longest chain in general.

* إذا longest chain الموجودة = ← لازم الاسم ينتهي بـ ene.

* We always start by looking for the longest chain.

* I must give the double bond the least possible number.

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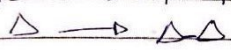
3 by-product ← Propane * مثلاً لو بدأنا بـ

cyclic → by-cyclo



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① = — = conjugated

② الكربون — تفصل بين 2 = isolated / non-conjugated

③ == Cumulated (? Alenes)

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* We always start by looking for the longest chain.

* I must give the double bond the least possible number.

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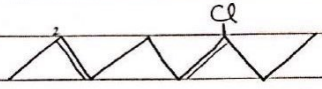
eg.

$$CH_3CH(CH_3)-CH_2CH=CH-CH_2CH_2$$

hept-3-ene أو -3-heptene لـ

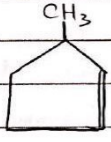
6-methyl-3-heptane

eg.



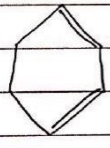
6-chloro-2,5-octdiene

eg.



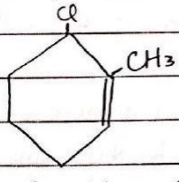
3-methylcyclopentene

eg.



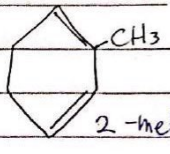
1,3-cyclohexdiene.

eg.



6-chloro-1-methylcyclohexdiene

eg.



2-methyl-1,3-cyclohexdiene

Note :> → 1 = octene
2 = octdiene
3 = octtriene
4 = octetriene

Note :> → [monosubstituated cycloalkene]:
* If there is one = in cyclic there is no need for writing # 1.
* The first & second carbons are on the =.
* The Sub takes the least Possible #.

Notes :> → 1 = & 2 sub
ال = دائماً رقم 1.
* The closest sub to the = must have the least possible #.
* If the = was in the middle ; depend on the alpha order.

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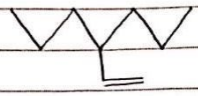
eg.

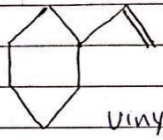


4 - vinylheptane

* ال sub يحتوي فقط على = vinyl

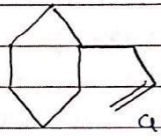
$H-\underset{\text{root}}{C}=\underset{\text{vinyl}}{CH_2}$

eg.



vinylcyclohexane

eg.



allylcyclohexane

Note:) $\underset{\text{root}}{CH_2}-CH=CH_2$

allyl

CH_2 مع CH_2 والارتباط في = ه

*

vinyl chloride

* Alkines :

eg. $CH_3C\equiv C-CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

6, 6 -dimethyl -2 -heptane

Note:) * we give the least possible # for the ≡

* en is written before yne (alphabetical order)

* We stick with least possible # for the first functional group.

eg. $CH\equiv C-CH_2CH_2\overset{CH_2CH_3}{C}=CH-CH_3$

5-ethylhept-5-en-1-yne

* إذا كانت 2 Congest chain ، واحدة فيها = أقرب الى فيها =

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غير مطلوب ≡ as a sub

eg.

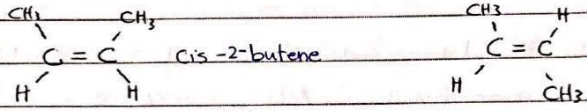
$CH_3-C\equiv C-\overset{Cl}{\overset{|}{C}H}-CH_2CH=CH-CH_3$

5-chlorooct-2-en-6-yne

*إذا تساوى العدد لـ = و ≡ نعتمد على alpha order إذا لا en أقل رقم.

3.5 Cis-trans isomers in alkenes:

cyclo alkanes — alkenes

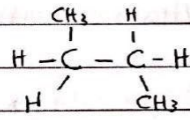


cis-2-butene — trans-2-butene

→ stereoisomers → configurational

Cis-trans: تستخدم لوصف مجموعتين

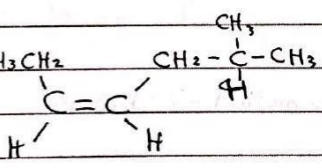
* في هذه الحالة فقط: di-substituted alkenes (مجموعتين غير H) استخدم cis/trans



* تعتمد المجموعات بالدوران لذلك هي في تغير مستمر لذا لا نستخدم cis/trans

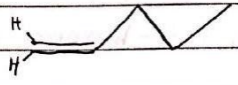
* أما في ≡ الـ pi لأنها تحتاج 180° ، درجة دوران الغرفة ليست كافية لأنها الـ adjusted = المجموعات على (Fixed).

eg.



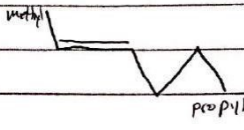
cis-6-methyl-3-heptene

eg.



no stereoisomers

eg.



* has stereo, we can use cis/trans beaz its disubstituted

trans-2-hexene

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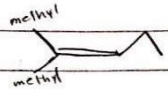
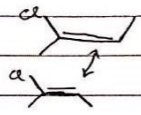
eg.



No stereo

eg.

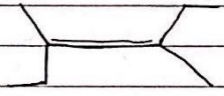


has stereo

* can't use cis/trans bcuz its tri-sub

* إذا الكربونات عليها نفس المجموعات ← ليس لها stereo
(يعني عن الاقل كربونة منهم عليها بنفس المجموعة ← ليس لها stereo)
* الكربونات على المجموعتين

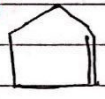
eg.



has stereo

* can't use cis/trans cuz its tetra-sub

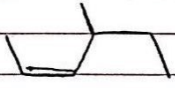
eg.



cyclopentene

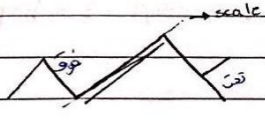
* في الحلقات الصغيرة (أقل من 13) لا نستطيع
على trans فقط Cis

eg.



cis-4-methyl-2-hexene

eg.



trans-2-methyl-3-hexene

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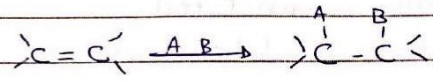
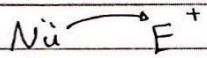
3

3.6 polar addition: has two species : 1) Elettrophile
تفاعل مرتبط بـ = و ≡ 2) Nucleophile



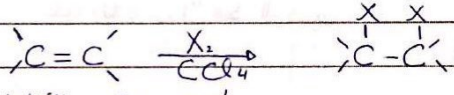
Notes:- *Phile mean seeker / محب / تائق

* electrophile → loves the charge of e^- → has positive E^+
* nucleophile → looks for the charge of nuckas → neg أو عنصر زوج e^- Nü



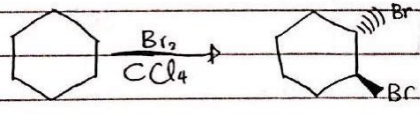
كثافة الكترونية تفضيل الكثافة الالكترونية

1 Halogenation of alkenes :



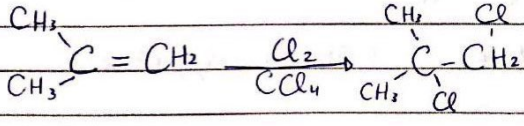
مذيب مناسب للتفاعل

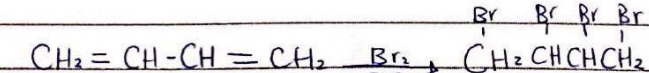
$X_2 = Cl_2, Br_2, I_2$



trans

* الإضافة تكون على شكل trans





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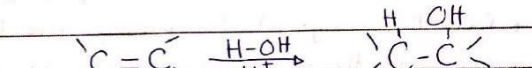
* Stoichometric amount
حسب المولات

* used as a synthetic rxn
test rxn to see if alkenes exist.

Br_2 + alkene ⟶ not red
Red colorless (there is a =)

[2] addition of water

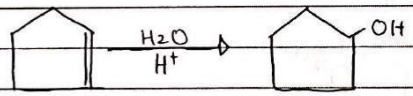


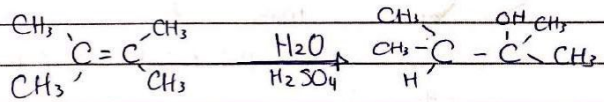
* في إضافة H_2O إلى الكين تضاف H إلى C و OH إلى C أخرى ودائماً" الناتج كحول.

* لا يتم التفاعل إلا بوجود H^+
acid catalyzed reaction

We add the acid in a catalytic amount
كمية قليلة جداً" فقط للتحفيز.

H^+: H_2SO_4, H_3PO_4





* هنا إضافة H و OH ليست trans.

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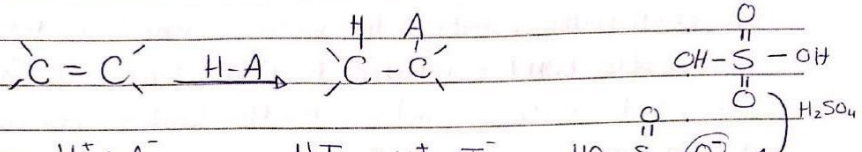
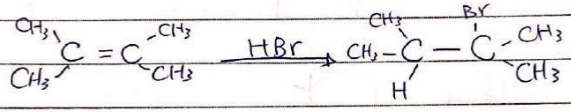
3 addition of acid to alkenes

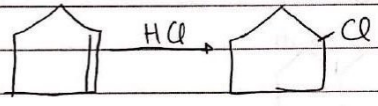


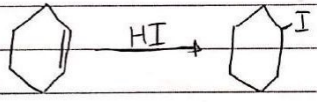
$HA \rightarrow H^+ + A^-$ $\quad$ $HI \rightarrow H^+ + I^-$

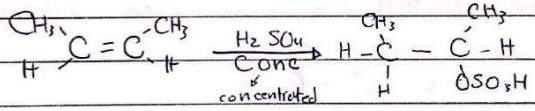
$HCl \rightarrow H^+ + Cl^-$ $\quad$ $H_2SO_4 \rightarrow H^+ + HOSO_3^-$

$HBr \rightarrow H^+ + Br^-$

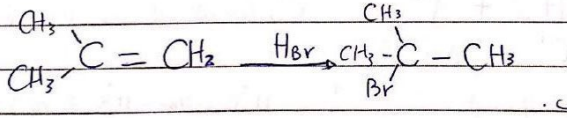




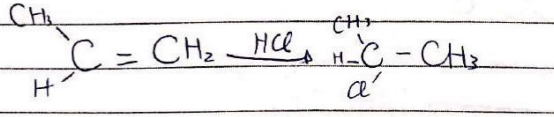




* كل الأمثلة السابقة symmetric.



* وهذا قاعدة ماركوفنيكوف.



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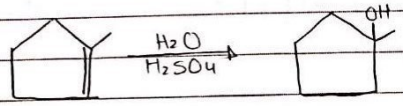
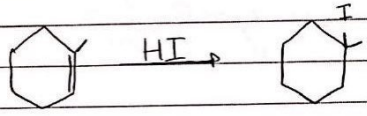
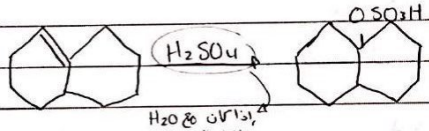
Note :) → adding acids is based on Markonikov's rule :
in electrophillic addition the proton is added to the carbon of the double bond connected to more hydrogens & the conjugate base is added to the carbon connected to less hydrogens or more substitited carbon.





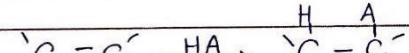


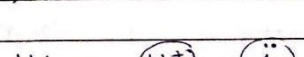
إذا كان في H_2O
يضاف ال H_2O

= ← بدل Nü يتفاعل E

3.9 electrophilic addition

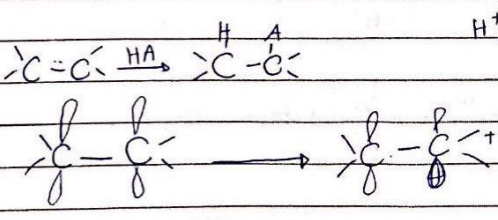
إضافة X2 أو HX بوجود حمض





*أي أيون عندما يتحلل يكون الـ Nü, E^+

*رابطة = H^+ ع — تهجم على H^+



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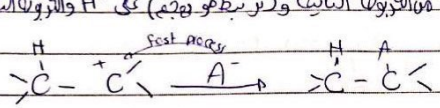
3

① كسر وتكوين Pi

② (تكوين)

* الكربونة تأخذ الالكترون من الكربونة الثانية و(ترتبط هو تهجم) على H^+ والكربونة الثانية تهجم موجبة

Nu^- يهجم على C^+



carbocation

* الـ carbon cation (very reactive) يجذب كل Nu^-.

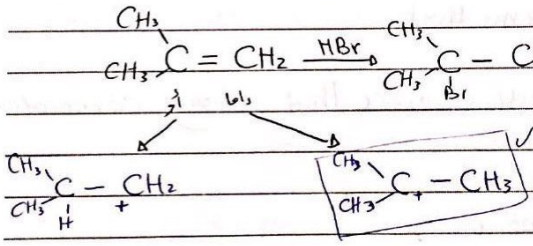
* الماء Nu^- ضعيف

* Mutlisteps mechanism → there is always a slower step → its the rate determinig step.

* الخطوة الأبطأ هي التي تحتاج طاقة أكبر

* The first step here is slower (rate detemining step) because it requires breaking a bond.

* لماذا هاركو ؟!



* 1° carbocation (لا يتفاعل)

3° carbocation (يتفاعل)
↓
Product ينتج
↓
لانه أسهل للتكون واسع
↓
more stable لانه
↓
less activation energy
↓
faster reaction

* لان هذه هي الخطوة المحددة للسرعة فكلما كانت اسرع كان التفاعل اسرع

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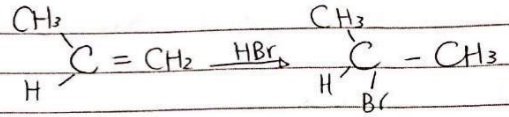
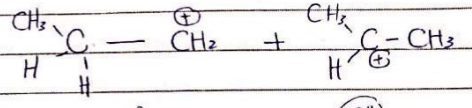




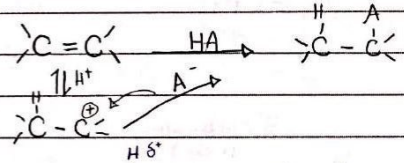
1° 2° ✓ more stable
faster to be formed

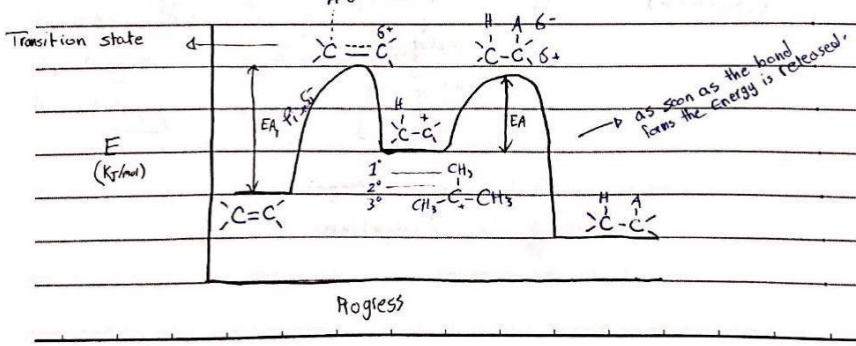
∴ more stable more H الي تكون carbocation.

*H يروح على الكربونة اللي عليها

* stability of carbocation
3° > 2° > 1° > methyl

* there is no actual evidence that primary carbocation actually exists because its unstable.





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Notes:) ⇒ * The formation of carbocation starts with absorption of energy & ends with release of energy.

* The formation of carbocation is associated with release of energy.

$E_{A1} \gg E_{A2}$

↓

this step is slower

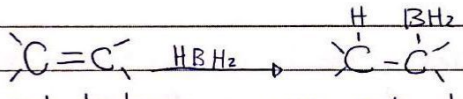
* It gives less energy when it forms 3°.

compound + H^+ ⟶ Carbocation

* إذا طلب رسمة ⟵ المطلوب ال most stable

* الأكثر استقراراً ⟵ 3° / الأقل استقرار 1°.

3.13 Hydroboration of Alkenes

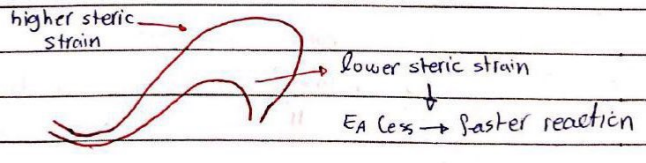


* One gets hydrogen — one gets boron

$$3\,CH_2=CH_2 + BH_3 \longrightarrow (CH_2-CH_2)_2-B$$

$$CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{B}}-CH_2CH_3$$

* عشان القدرة يعطي 3H إلى 3 alkenes وعشان القدرة على الارتباط بـ 3.



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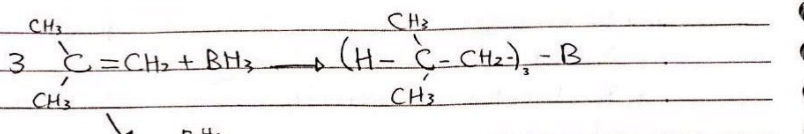
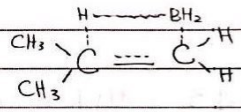


anti-MarKounitro's

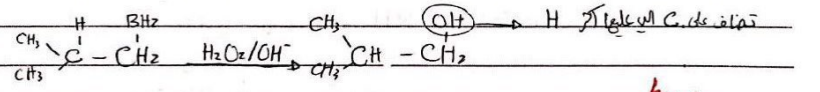
* التفاعل الوحيد الذي يشتغل عكس ماركو ⇐ Not ok

* its a one step reaction that has one transition state. & no intermediates
* its not an electrophile addition
* in one step borain attaches to the → double bond

B-H broken
H-C formed
B-C formed
C-C broken

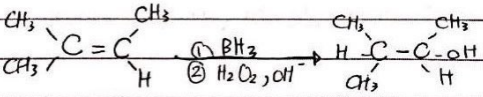


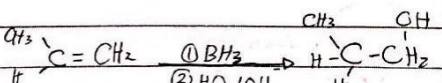
* BH_2 choose the C with more hydrogen because there is lower energy this way.
* all hydroboration reactions are anti-MarkounKor's



تمتاز على C اليمين لأن H

hydroboration then Oxidation





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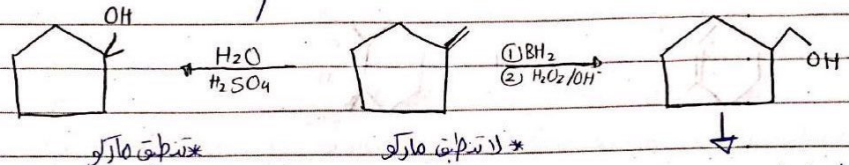
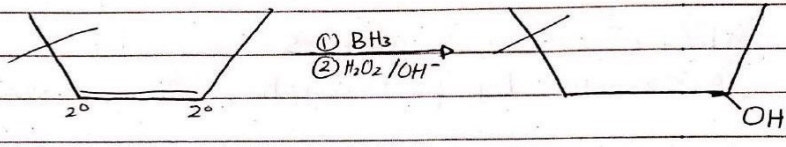
This way I cant form primary alcohol because primary carbocation won't be formed



*تنطبق ماركو
* تعمل ل more stable carbocation

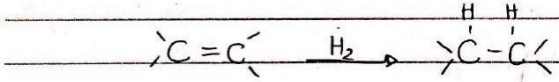
* لا تنطبق ماركو
* تعمل لاقل stric strain

primary alcohol

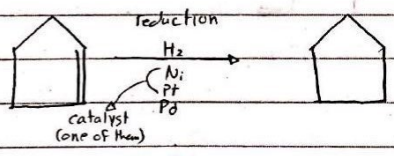


* OH goes to : the carbon that is connected to smaller groups (less steric strain)

3.14 addition of hydrogen :

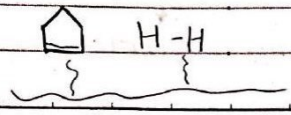


هدرجة
اتباع بـ H



* Why we use Ni/Pt :

- alKenes have low boiling points / H is a gas.
  ↑ Pressure ⟶ causes problems
- they meet on a metal surface, alKenes & H_2 are absorbed on the Surface ⟶ less space ⟶ less E_A ⟶ reaction happens in one step.



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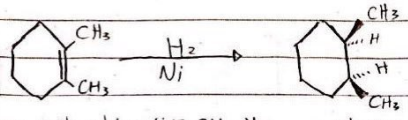


Cis

دائماً Cis لأنه بينضاف على وجه واحد ← ال 2H تنضاف خطوه واحده مره واحدة

GOOD NEWS ⟹ ~~3.15~~ و ~~3.16~~ ملغي :)

3.17 Oxidation & alkenes

ⓐ Oxidation by pernanganate

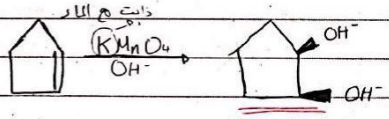
مهم مكرر دائماً في الامتحان

$$\text{>C=C<} + KMnO_4 \xrightarrow{OH^-} \text{>C(OH)-C(OH)<} + MnO_2$$

red ppt → inorganic products

* this reaction is a test reaction

If we had a red ppt → there is an alkene



Cis

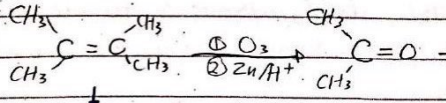
الذرتين اللي بيعملوا

ⓑ Ozonolysis

$$\text{>C=C<} \xrightarrow[\text{② } Zn, H^+]{\text{① } O_3} \text{>C=O} + \text{O=C<}$$

acetic acid — carbonyl

* نوعية وعدد ال products يعتمد على ال Sub اللي كانت على ال alkene



Symmetric — one Ketone product

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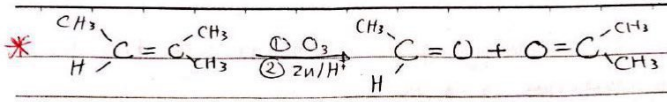
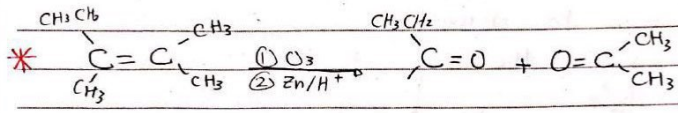
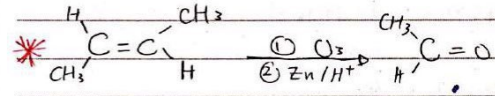
3



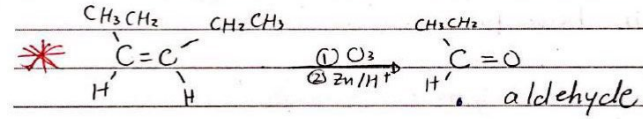
• aldehyde Ketone



• 2 Ketones



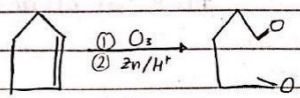
• aldehyde

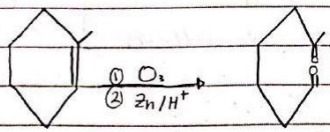


• aldehyde

* Ozonolysis for cyclic alKenes :

* ارسم الـ compound كما هو دون = بعدين مكانه
الـ = أرسم O O
* ينتج compound واحد بمجموعتين كربونيل.





• give the shape of hydrocarboin compound that reacts under ozonlsis to give _____

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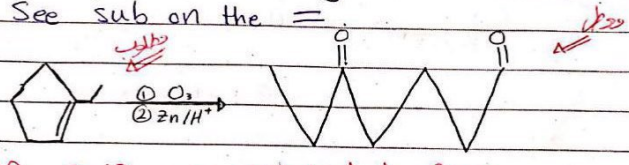
Notes:→ * If we had 2 carbonyl groups in the product then the starting material is cyclic.

خطوات معرفة الاصل من الناتج

* We know the size of the cycle by counting C between the carbonyl group.
* put = in the drawing.
* See sub on the =

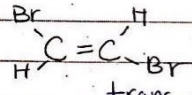
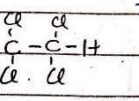


3.18 3.19 → explained before:)

3.20 addition reactions to alkynes:

* alkynes & alkenes react in a similar way because they both have pi.

* Halogenation of alkynes:

- $H-C\equiv C-H + 1\,mol\ Br_2 \longrightarrow$ 
  trans-dibromoalkene
- $H-C\equiv C-H \xrightarrow{Cl_2\ excess}$ 

- 1 mol → trans-dibromoalkene
- excess → tetra bromo, tetraiodo alkan

الناتج يتحدد حسب كمية X_2

* Hydrogenation of alkynes:

$$CH_3C\equiv C-CH_3 \xrightarrow[N_2]{H_2} CH_3CH_2CH_2CH_3$$

أي = أي ≡ يحولها الى single , اغا

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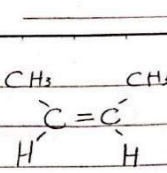
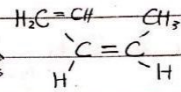
3

$CH_3C \equiv C-CH_3 \xrightarrow[\text{Lindlar's}]{H_2}$ 

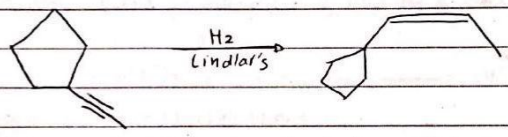
يتفاعل فقط مع الـ alkyne ويحول alkyne فقط إلى cis-alkene

cis-alkene → stereospecific

* stereospecific reaction → a reaction that results in sterei somers

$CH_2=CH-C\equiv C-CH_3 \xrightarrow[\text{Lindlar's}]{H_2}$ 

الحل → * أرسم الـ = (التي نتجت من الـ ≡)
ثم أكمله على شكل cis .



* Addition of Hydrogen halide : (electrophillic addi

Mako يطبق

- $CH_3C \equiv C-H + 1\,mol\ HCl \longrightarrow CH_3\overset{Cl}{C}=CH_2$

- $CH_3CH_2C \equiv C-H \xrightarrow[\text{excess}]{HBr} CH_3CH_2\overset{Br}{\underset{Br}{C}}-CH_3$

$\xrightarrow{HBr} CH_3CH_2\overset{Br}{C}=CH_2 \xrightarrow{HBr}$

- $CH_3C \equiv C-CH_2 \xrightarrow[\text{excess}]{HCl} CH_3CH_2-\overset{Cl}{\underset{Cl}{C}}-CH_3$

* عند وجود excess ← يتحول إلى الكان وتكون الـ 2X على نفس الكربونة والـ 2H على نفس الكربونة سواء كان المركب symmetric أو لا .

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• $CH_3CH_2C\equiv C-CH_3 \xrightarrow[\text{excess}]{HBr} CH_3CH_2CH_2\overset{Br}{\underset{Br}{C}}-CH_3$

$+ \; CH_3CH_2\overset{Br}{\underset{Br}{C}}-CH_2CH_3$

* Addition of water : تطبق ماركو / لا تقبل إضافة المزيد من الماء

يقبل جزيء واحد

$CH_3C\equiv C-H \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3\overset{OH}{C}=CH_2$

enol

*يكون ال enol في حالة توازن مع مركب آخر في عملية تسمى tuatarization

$CH_3\overset{OH}{C}=CH_2 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

enol

* more stable (Keton form) a seton

*الكربونة إلي عليها more H ← تأخذ H و

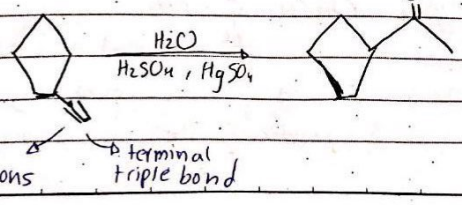
*الكربونة no H ← $\overset{O}{\overset{\|}{C}}$

• $CH_3CH_2C\equiv C-H \xrightarrow[H_2SO_4, HgSO_4]{H_2O} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

• $CH_3CH_2C\equiv C-CH_3 \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_2CH_3$

$+ \; CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

*إذا جي سؤال عليه و وضع بهم واحد فالجواب هو Ketone (more stable)



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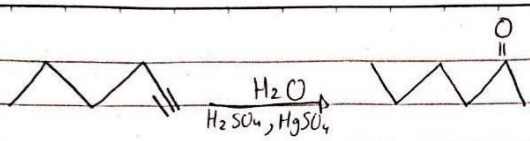

3.21 Acidity of alkynes :

$CH_3C \equiv C-H + NaNH_2 \xrightarrow{NH_3} CH_3C\equiv C^- : Na^+ + NH_3$

acidic — terminal H — Strong base — Na

تفاعل يحدث على حرارة منخفضة بحيث NH_3 سائل

astlyde anion (alkyne with a minus)

alkyne + strong base ⟶ : عليها C في alkyne

* Which of these compounds is the most acidic :

• $CH_3-C\equiv C-CH_3$ ✗ / $CH_3C\equiv C-H$ ✓

imp. MCQ

* Acidity :

$-\overset{|}{\underset{|}{C}}-H < >C=C<^{H} < C\equiv C-H$

C-H sp^3 — C-H sp^2 — CH sp

$C_{sp^3} < C_{sp^2} < C_{sp}$ in E.N

more spherical ⟶ تجذب e أكثر

• eg : O-H C-H

more acidic H

because O is more E.N than H

more polar bond

bigger partial + charge on H

* كلما كانت ال δ+ على H أكبر يكون more acidic

أي كلما كانت الذرة التي ارتبطت بها H more EN

$C_{sp^3}-H^{\delta+} < C_{sp^2}-H^{\delta+} < C_{sp}-H^{\delta+}$

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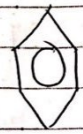
CH.4 Aromatic compounds :

Benzene C_6H_6 Kekule's 

* يرسم المركب بهذا الشكل كأنه الأكين X 1, 3, 5-cyclohexatriene

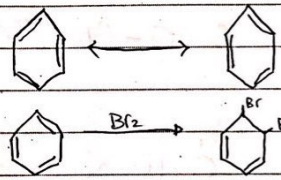
له مركب غير موجود والشكل غير موجود فعلياً

في البنزين نستخدم رسمة 1,3,5 cyclohexatriene

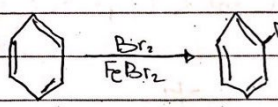
لل Benzene لتسهيل الفهم.

له كل روابط البنزين لها نفس الطول ونفس الطاقة

* البنزين ليس له Resonance فعلياً



* البنزين لا يتفاعل مع Br_2 إلا اذا وضعنا $FeBr_2$ و عند ما يتفاعل يكون تفاعل Substitutional وليس addition } الفرق بين الأكين و بنزين



substitution

* نوع التهجين في ال C هو SP^2 (لأن كل ذرة 3 مجموعات)

- كل ال 6 Porbital تعمل side to side overlap } Closed Pi sys. ← Because its a cyclic compound

- كل ال Porbitals على نفس المستوى وما يساعد في ترابطهم هو أن البنزين planar

* كل مركب فيه 6 π e يتصرف كـ aromatic وليس كأكين أي لا يتفاعل addition

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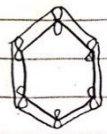
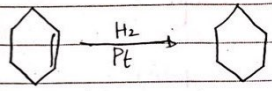


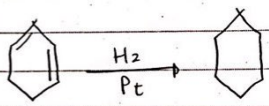
cyclic planar

① cyclic
② planar
③ $6\pi e^-$

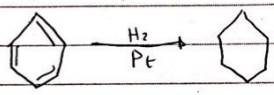
} ⇒ عندما تتواجد هذه الصفات يكون في المركب صفة الـ aromaticity
more stability



$\Delta H = -28.6$ Kcal/mol



$\Delta H = -55.4$ Kcal/mol

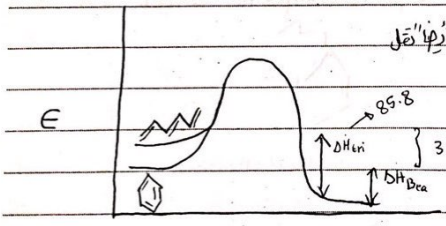


$\Delta H = -49.8$ Kcal/mol

* لو عاملنا البنزين أنه فيه 3 isolated pi systems بيعطيني :

$3 \times (-28.6) = -85.8$ Kcal/mol
$+ 49.8$
-36 Kcal/mol

* عندما تقل ΔH محتواها الـ starting material أيضاً تقل



* resonance energy
* Stability energy
لس البنزين

Benzene has the most of this energy (most stable.

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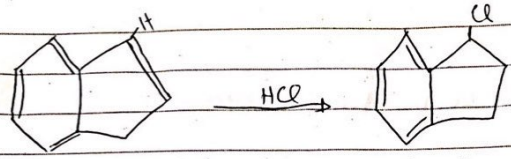
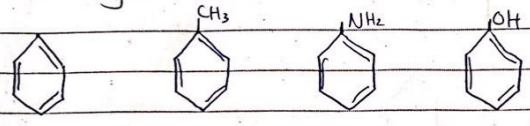


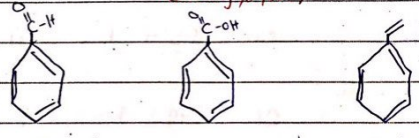
4.6 Naming of aromatic compounds :

(mong)

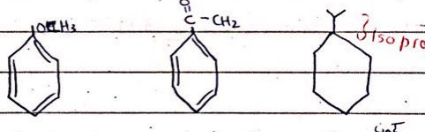


benzene toluene aniline phenol

(cleaning, dyes -)



benzaldehyde Benzoic acid stylene (polstrene -)

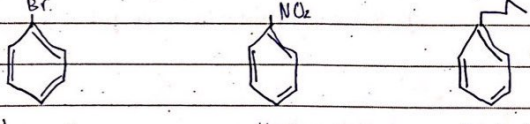


المجموعة الاولى

isopropyl

anisol acetophenol Cumene كومين

benzene + sub اسم الـ compounds باقي الـ :



bromobenzene nitrobenzene butylbenzene

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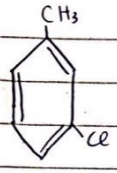
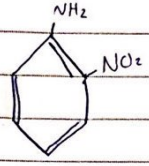
Disub



3-Chlorotoluene

m-chlorotoluene

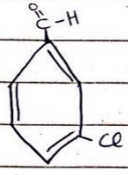


2-nitroaniline

O-nitroaniline

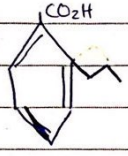
4-bromophenol

p-bromophenol



3-ethylbenzablehyde

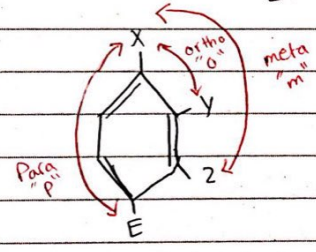
m- " "



2-propylbenzoicacid

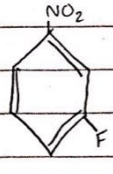
O- " "

* المجموعة الاولى في حالة الـ disub : اذا إجا نفسه مع sub يسمى باسم sub مع الاصلي



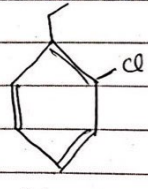
* طريقة الاولى تستخدم فقط في الـ benzen الـ disub .

* مركب لا ينتمي للمجموعة الاولى



1-Fluoro-3-nitrobenzene

m-Fluronitrobenzene



1-Chloro-2-ethylbenzene

O-Chloroethyl benzene

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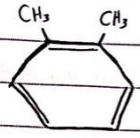
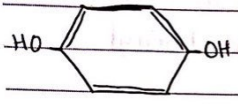
3



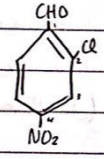
1,2 - dimethylbenzene
O - exylene
O - dimethylbenzene

disub
* عندما يتكرر الـ sub دون
وجود أولوية للاسم
نعتمد على اسم الـ sub.

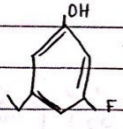


1,4-dihydroxybenzene
P - dihydroxybenzene

Trisubstituted :

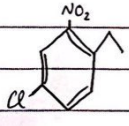


* دائماً المجموعة صاحبة الاولوية موقعها رقم 1
2-Chloro-4-nitrobenzaldehyde



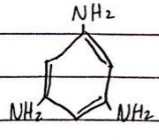
* اذا من الجهتين يعطي نفس الارقام للـ sub فاعتمد على الـ Alpha
3-ethyl-5-Fluro phenol

* مجرد ما انوجد على البنزين مجموعة كيتون فإنه المركب يعامل معاملة الكيتون



E 1 2 4
NO_2 1 2 5
Cl 1 3 4
4-Chloro-1-ethyl-2-nitrobenzen

* Tri-Sub with no priortey for any of them.
* regardless for any alpha here we look for least Possible #.



1,3,5-triaminobenzene

- Trisub with the same Sub

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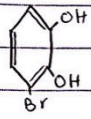
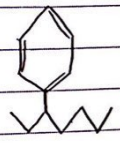


1-bromo-2,3-dihydroxybenzene

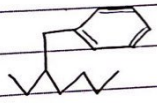
*alphabatical order

* Benzen as a sub is called Phenyl.



3-Phenylheptane

*عندما يكون أول السلسلة (المتفرعة من البنزين) 4 أو أكثر تستطيع اعتبار البنزين هو الرئيسي (حيث يعتمد الاسم الاسهل)

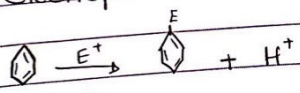


3-benzylheptane

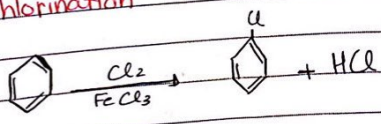
عندما يكون بنزين عليها CH_2 تسمى benzyl
(مثل فكرة الـ allyl)

4.8 Electrophillic Aromatic Substitution

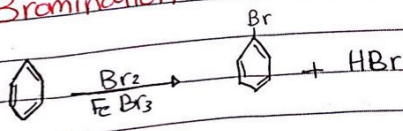
عنوان product / reagent هو يعني كل واحد



[1] Chlorination



[2] Bromination



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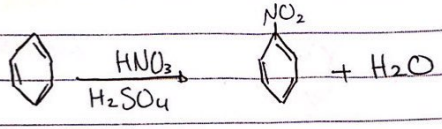
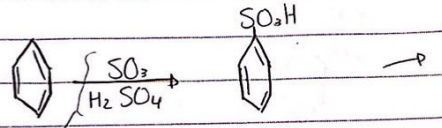
3 Nitration



4 Sulfonation



* عندما تبدل H بـ NH_2 يستخدم الناتج كمضاد حيوي

Fumming Sulforic acid

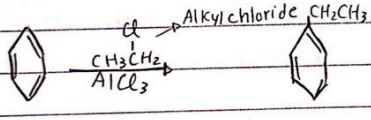
متبع بـ SO_3

benzensulfonic acid

5 Alkylation

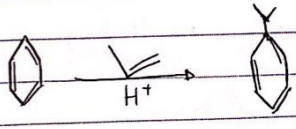
إضافة الكان

ⓐ Friedl - Craft Alkylation



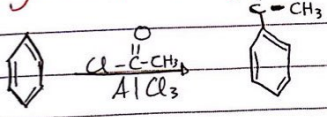
* يزوج الـ Cl ويضع مكانها البنزين

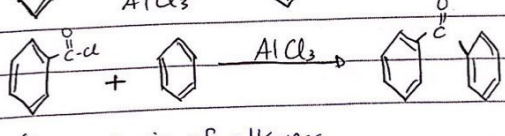
ⓑ



البنزين يضاف على C اللي عليها H less

6 Acylation (Acyl = carbonel)





طرق تحضير كيتون:

1. Ozonolysis of alkenes
2. addition of water to alkyne
3. Acylation

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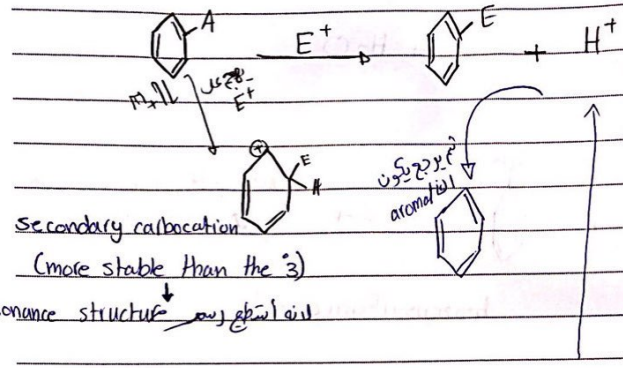
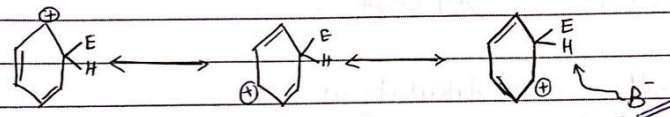
Benzen has:
1 π system / 6 π e⁻

4.9 The mechanism of electrophilic aromatic substitution

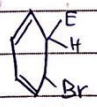




3 resonance structures for the carbocation
(more resonance structures → more stability)

بما انه في E^+

اذا في B^- يهجم ويزيل H ← يهجم على H ولا يكون Sub لانه ال aromatic مستقر اكثر من



لا يتم تكوينه

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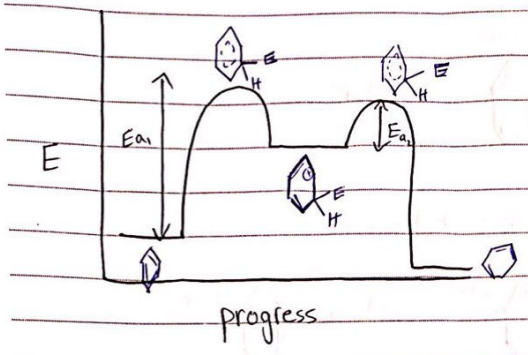
Scanned with CamScanner



$Ea_1 \gg Ea_2 \longrightarrow$ كسر رابط من C إلى H

لأنه كسر لـ aromatic — وتنتقل من less إلى more stable

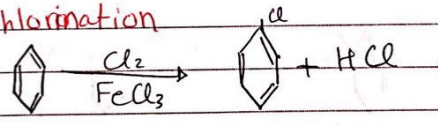
إذا هي أقل — سرعة التفاعل: هنا تعتمد على stability starting material

* benzen ring more e^- rich (e^- giving group) $\longrightarrow$ تنافر أكثر لأن الكثافة لـ e^-

$\longrightarrow$ أقل استقرار $\longrightarrow$ ترتفع الـ energy $\longrightarrow$ تقل Ea $\longrightarrow$ تفاعل أسرع

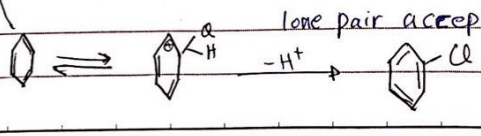
* If the sub was withdrawing e^- then the rxn is slower.

I Chlorination



$\overset{\delta+}{Cl} \rightleftharpoons \ddot{Cl}: + FeCl_3 \rightarrow E^+$ ← كل الـ system

lone pair of e^- — lewis acid — lone pair acceptor



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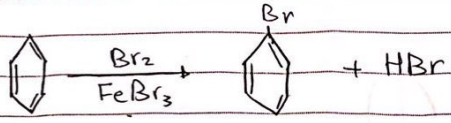
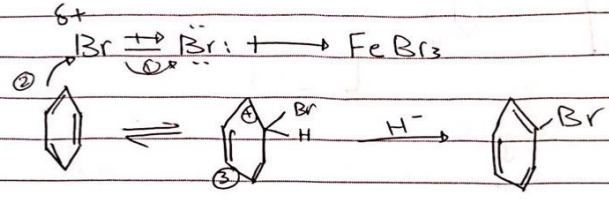
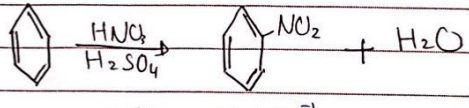
2 Bromination





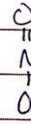
3 Nitration



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

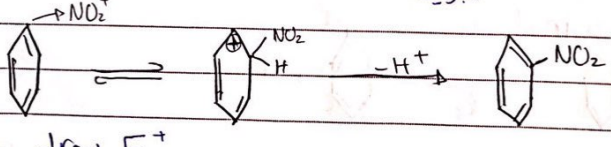
$H^+ + HNO_3 \longrightarrow NO_2^+ + H_2O$

Nitronium
هو الالكتروفيل



E^+

يشمل وجود E^+ لاجراء التفاعل



eg. draw E^+

eg. Which of the following is the E^+ of _____

eg. draw reasonance structers.

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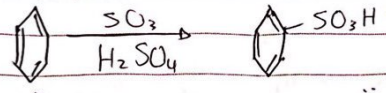
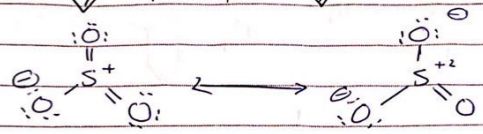
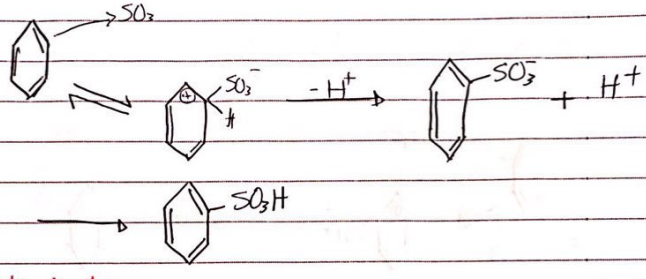
4 Sulfonation



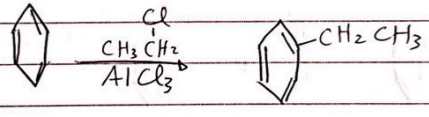


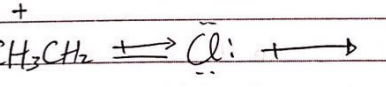
*في ال SO_3 ال S موجبة فتكون جاذبة للبنزين ليهجم عليها

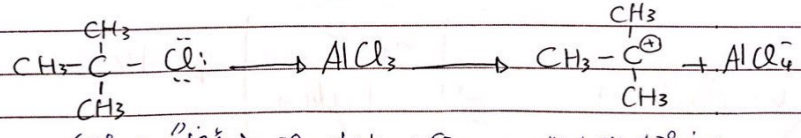


5 Alkylation

ⓐ Friedl - Craft







*في alkyl Chlorit 3° ـــــ يتكون 3° carbocation (وأيضاً في ال 2°)

*في ال alkyl chlorid 1° ـــــ تدث إزاحة فقط

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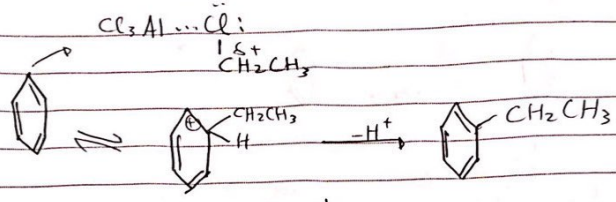
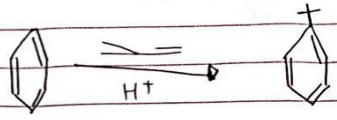
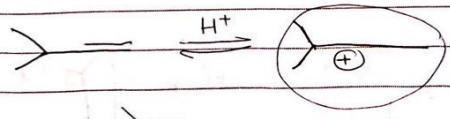
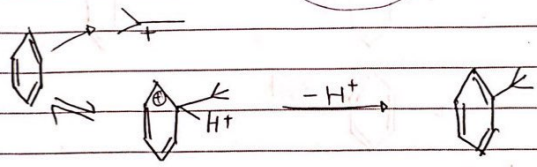
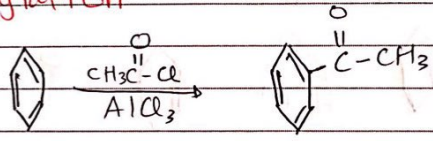


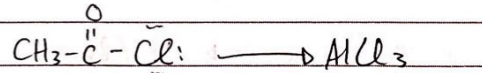






6 Acylation





(ك + هو الـ Cl الزائد)

E^+ $\boxed{CH_3\overset{+}{C}=O \text{ Acylium}}$ + $AlCl_4^-$

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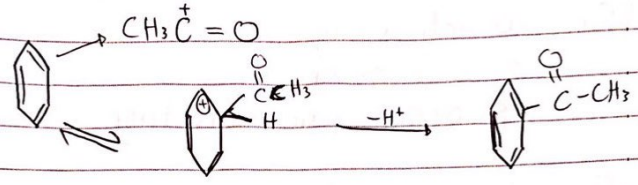
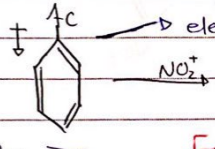
Scanned with CamScanner



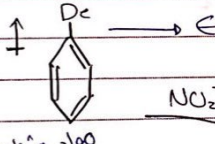
4.10 Activating & Deactivating Groups



→ electron releasing Group (ERG) → the benzen becomes e^- rich → stability of ring increases → E_a decreases

مواد منشطة → اذا كان عليه تكون سرعة التفاعل اعلى من البنزين

Faster reaction



→ Electron with drawing Groups (EWG) → they withdraw e^- density from the ring → more stable ring → more E_a → slower reaction

مواد منشطة تسبب سرعة التفاعل

slower reaction

① Reactivity
② product

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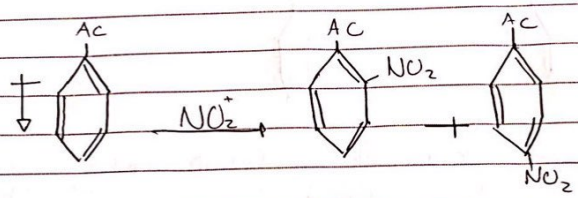
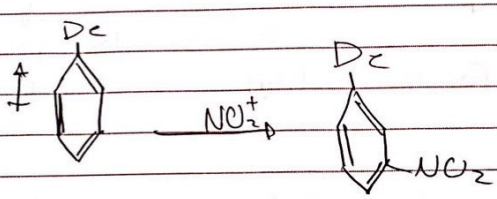
AG ① activating
② e-relesing
③ ortha - para directing

DG ① deactivating
② e^- withdrawing
③ meta - directing groups





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No.

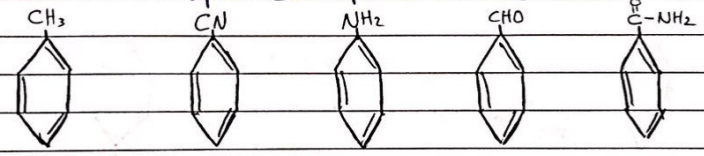
Table 4.1

reactivity increases

$-\ddot{N}H_2$, $-\ddot{N}HCH_3$, $\ddot{N}(CH_3)_3$	most reactive activating o, p-directing groups
$-\ddot{O}H$, $-\ddot{O}CH_3$	
$-\ddot{N}H\overset{O}{\overset{\|\|}{C}}-CH_3$	
$-CH_3$, $-CH_2CH_3$ مشتقة لكن ليس عليها أزواج	
$-H$	
F, Cl, Br, I * high E.N	deactivating m-directing group
$\overset{\delta+}{-}\overset{O}{\overset{\|\|}{C}}-CH_3$, $\overset{\delta+}{-}\overset{O}{\overset{\|\|}{C}}-H$, $\overset{\delta+}{-}\overset{O}{\overset{\|\|}{C}}-OH$	
$\overset{\delta+}{-}\overset{O}{\overset{\|\|}{C}}-NH_2$, $\overset{\delta+}{-}\overset{O}{\overset{\|\|}{C}}-OCH_3$	
$-\overset{+}{S}O_3H$	least reactive
$-\overset{\delta+}{C}N$	
$-\overset{+}{N}O_2$	

* halogenes are deactivating because of their high E.N but they are ortho, para directing groups → لأن لديها كثافة عالية

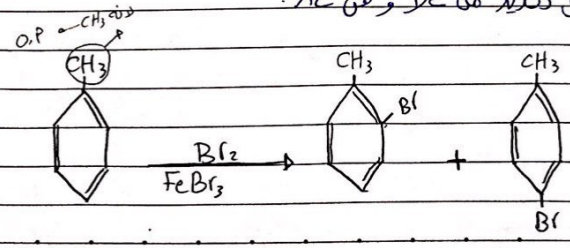
* Rank the following compounds according to their reactivities upon electrophilic atomic substitution:



I	II	III	IV	V
Ac	De	Ac	De	De

III > I > IV > V > II

* أول خطوة في الحل تحديد من De ومن Ac.



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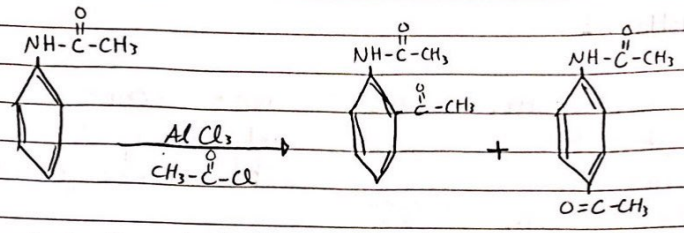
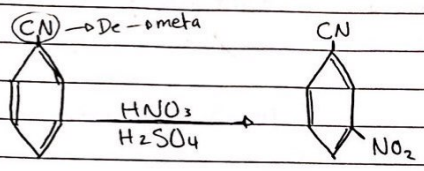
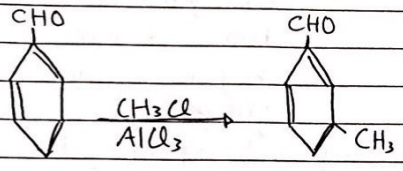
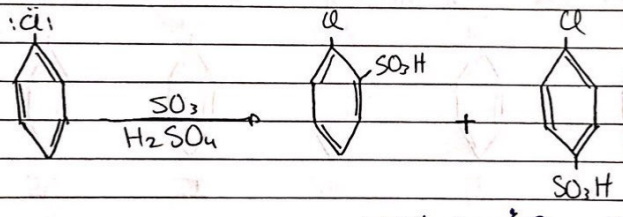


* الوجبة التفاعل في المجموعة الأصلية على البنزين (الالكتروفيل مجرد تابع يتم توجيهه)







* طريقة ٢ : ① أحدد نوع التفاعل.

② أحدد الموقع من خلال المجموعة AC/DC الموجودة على البنزين

• Here check the book p.g 130, 131, 132, 133
For the Next Notes (Just an advice) :)

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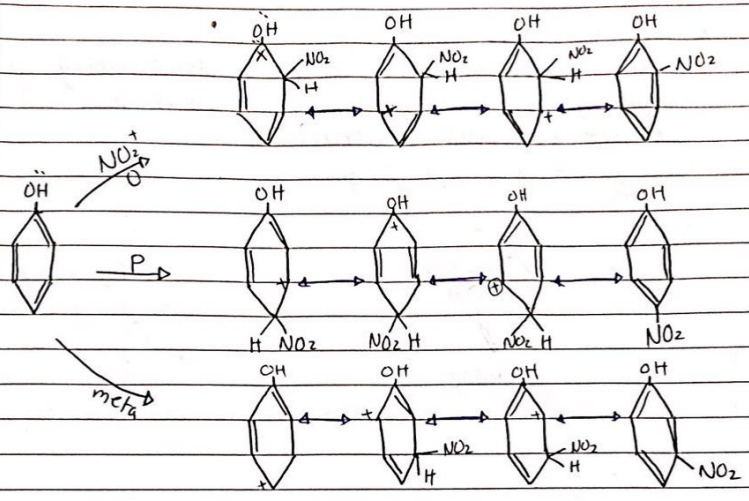
No.



* ال reaction في حالة ال AC يكون more stable carbocation في حالة O/P فالتفاعل أسرع.

* التي يزيد ال stability هو زيادة عدد ال reasona structures

* ال activating groups لأنه عليهم long pair of e⁻ يرسمون reasonance structure إضافي

↓

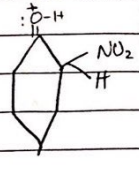
more stable carbo

↓

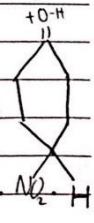
Faster reaction

* The extra structure we drew is the most stable because all its atoms follow octet rule.

O: most stabele



para : most stable



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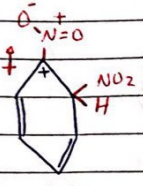
No.

* Why halogens O/P ?
- Cl has high E.N so its a deactivating group but it has lone pairs of e^- so it has one more reasonance structure.

* في حالة الـ NO_2 D.G.S ← نفس الرسمات بدل OH نضع NO_2

حالة O :

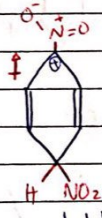


unstable

* هنا المجموعة تسحب الـ e^- مما يجعل الحلقة أكثر موجبة وأقل استقرار

* إذا فعلياً في حالة الـ O عندي 2 structures

حالة P :



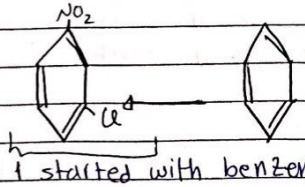
unstable

* في حالة الـ meta
more reasonance structures يكون
↓
more stability

① حدد بشكل عام التفاعلات
② حدد m ، o ، p (نوعها حسب الـ directing) لكل مجموعة

آخر موضوع في الامتحانات :

4.12 The importance of O.P & m-directing groups



* if I started with benzene I have to do chlorination & nitration

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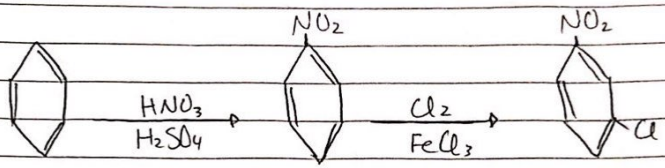
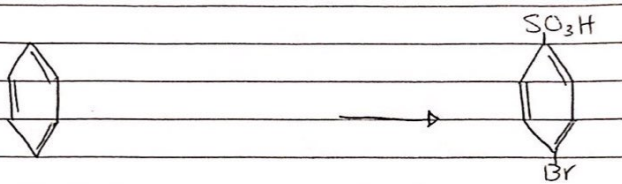
4

No.

* The Cl is o.p directing group
  NO_2 is m directing group



H.W



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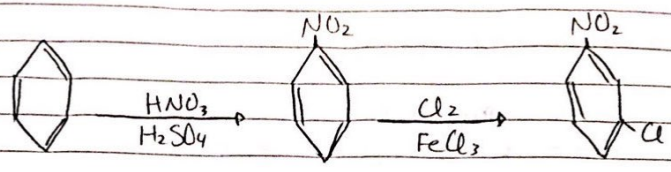
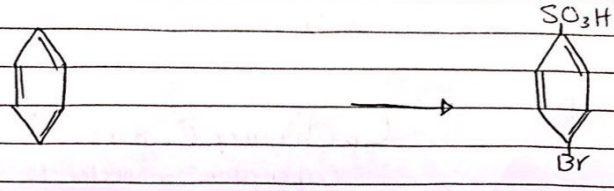
4+5

No.

* The Cl is o.p directing group
  NO_2 is m directing group



H.W



CHAPTER 5 : Stereochemistry

5.1 Chirality & enantiomers

* In this Ch. the condition for having isomers is Chirality.
* Chirality : Assymetry ⟶ the compound has no plair of symmetry.
* Enantiomer : a chiral compound + the mirror image of the chiral compound } enantiomers

Enantiomers :

geometry { ① Mirror images.
② non - superimposable (physically dont fit) البعد المقوس (ابعادهم المادية لا تطابق)

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No.

eg. The compounds that are mirror image & non-supeimposable سوال امتحان

① Cis-trans ② ~~~ ③ ~~~ ④ enantiomers

* Chemically speaking

- The compound has stereoisomers when it has → stereogenic center.

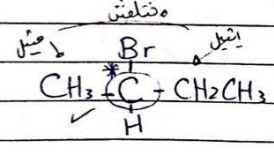
stereogenic Centre
- → double bond (Cis/trans) (تهجين sp^2)
- → Chirality Center: Carbon atom connected to 4 different groups.

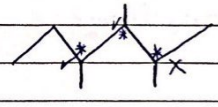
* When the two compounds don't fit physically then their atoms have different arrangements (ترتيب مختلف في الفراغ) then they are isomeres.

* When is the compound Chiral?

① Chirality Center (حتى يكون من ال stereoisomers)

② No plain of symmetry





2 Chirality centers
Chiral

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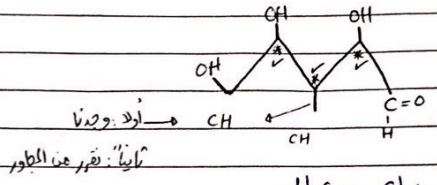
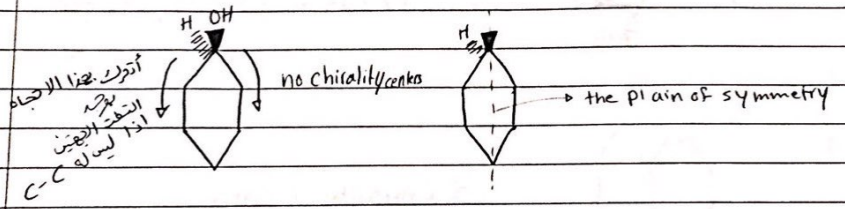
No.

* Finding condidates for chirality
  1. 4° carbon
  2. 3° Carbon
  3. 2° carbon connected to hetero atom not C, not H.
  4. 1° Carbon connected to 2 hetero atoms

* If there is no heteroatoms then forget about the 1°, 2°

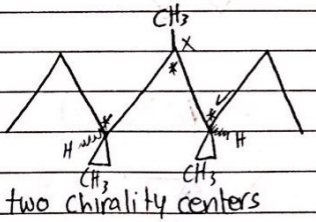


three Chirality Centers.



eg.

Chiral



two chirality centers

Achiral (bcuz it has a plain of symm.)

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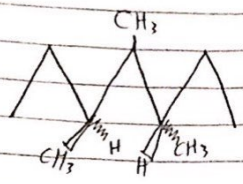
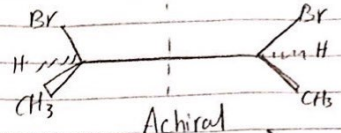
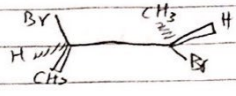
No



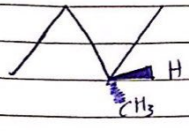
two chirality centers



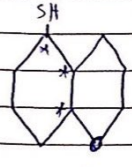
Achiral



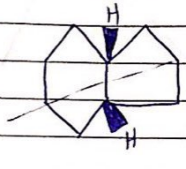
* حتى لو كان في لحظة من اللحظات كان المركب plain of symmetry
اذا المركب بكل ال conformers يكون A-Chiral



Achiral / has no chirality center

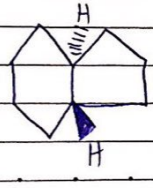


3 Chirality Centers



→ Plain of symetry

2 chirality centers Achiral



Chiral

* اختلاف ارتباط ال 2 hydrogens أدى إلى
اختفاء ال plain of sym

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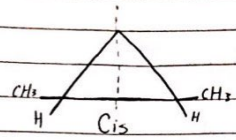
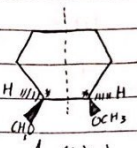
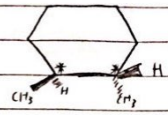
No.





A-Chiral

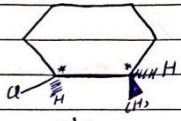


Chiral

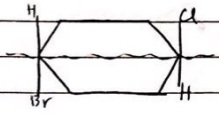
cyclic, di-sub, cis, same sub] always A-Chiral

because there is always a plain of symm

cis, different sub } Chiral
trans, same sub }

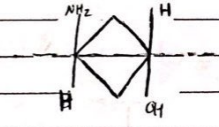


Chiral



* Achiral (always wether it was cis, trans same or diff sub)
* it has no chirality center (the C is shared)

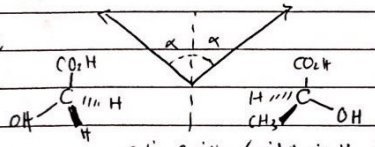
1,4-disubstituted cyclohexane



always Achiral
* No chirality center (second C is shared)

1,3-disubstituted cyclobutane

*mirror image



للرسم

* القريب قريب / البعيد بعيد / الداخل الداخل / الخارج خارج
↑ ↑ ↑ ↑ ↑ polarized light
(parallel to each other كل ما في) Notes :>

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No.

* every chiral is optically active
* every achiral is optically inactive

Optical Activity: كسر الضوء وحرفه

eg: which compound is Chiral / optically active

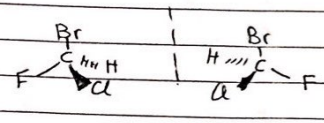
* الفرق الوحيد بين الـ enantiomers أن واحد منهم يحرف الضوء لليمين والآخر لليسار

- لليمين (+) dextrorotatory
- لليسار (−) levorotatory

• بنعمل الدرجة ← observed rotation ← تقاس بـ polarizo meter

S.R Configurations:

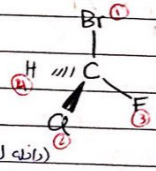
* We distinguish between the chirality centers by using S.R



Steps:

① Rank the groups around the chirality center from 1 to 4 according to the atomic number of the atoms, atom by atom.

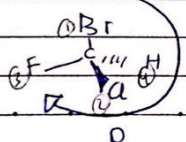
(إذا كانت المجموعات في المركب متعددة الذرات ← كل مجموعة نقارنها مع بعضها)



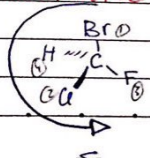
② Group 4 must be away from you (دائماً لبعد)

③ Turn around the chirality center starting from 1 to 2 to 3 by using curved arrow

anti-clockwise → S / clockwise → R



R



S

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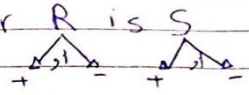
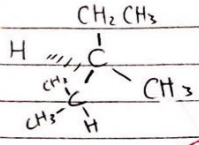
No.

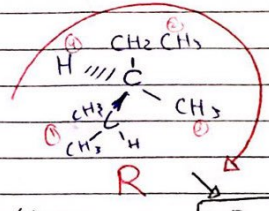
* mirror image / enatiomer for R is S



eg.



solu:



* we're looking for atom with higher atomic n

R

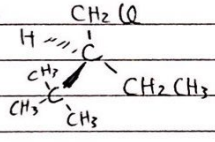
* R, S قبل cis / trans

لازم تظهر في الاسم في ال 3D

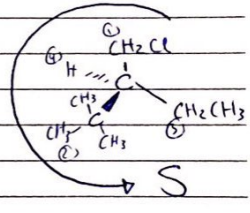
3R-2,3-dimethylpentane

no dash between them

eg.

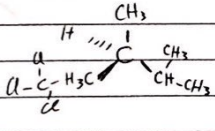


Solution

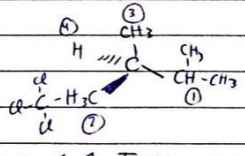


S

eg.

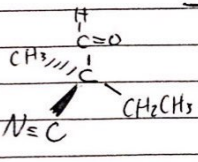


Solution

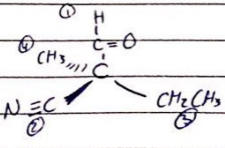


3R-1,1,1-Trichloro-3,4-dimethyl Pentane

eg.



Solution



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Scanned with CamScanner

No.

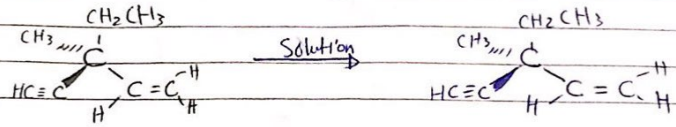
* اذا تساوت الـ 2nd atom نعتمد على أولية الروابط

$\equiv > = > -$

$-C\equiv C-$: $-\overset{C}{\underset{C}{C}}-\overset{C}{\underset{C}{C}}-$ / $>C=C<$: $-\overset{C}{\underset{C}{C}}-\overset{C}{\underset{C}{C}}-$

وكأنه

eg.



3S-3-ethyl-3-methylpent-1-en-4-yne

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S

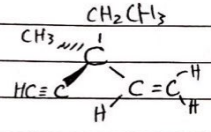
No.

* اذا تساوت ال 2nd atom نعتمد على أولية الروابط

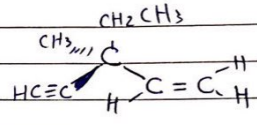
≡ > = > −

− C ≡ C − : وكافية / C = C : C − C

eg.

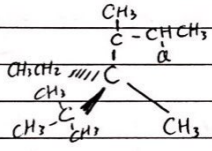


Solution →

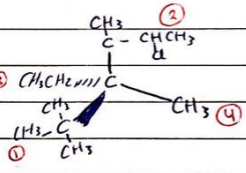


3S-3-ethyl-3-methylpent-1-en-4-yne

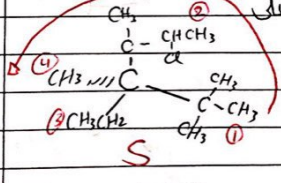
eg.



Solution →

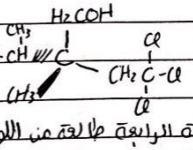


* مجموعة 4 هنا على مستوى اللوح ← لازم نعمل rotation ال compound بحيث مجموعة 4 تصير داخله في اللوح ← بتبقى المجموعة اللي في الاعلى

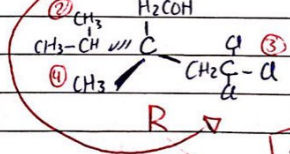


4S-4-t-butyl-2-Chloro-3,4-diethylhexane الاسم

eg.

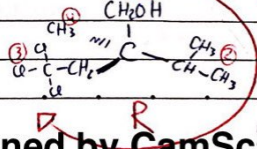


Solution →



* اذا كانت المجموعة الرابعة طالعة من اللوح استطيع التحرك عادي واطلع نوع ال config بعدين أعلى.

أو



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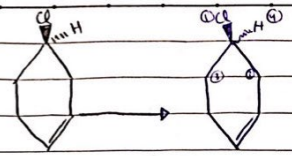
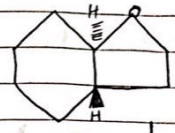
No.

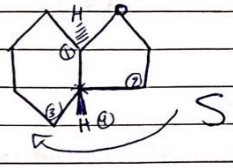
eg.



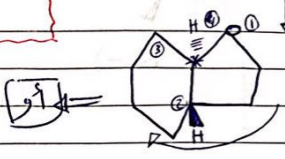
4R-4-Chloro cyclohexene

eg.





S

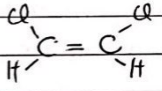


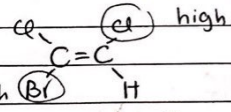
R

5.4 E,Z Convention:

stereogenic center ← cis/trans isomers

*الي بكون الها





high

high

* stereogenic center
* (di-sub alkene)
* Cis * Z

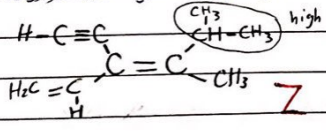
* stereogenic Center
* Can't use cis/trans (tri-sub)
* E

* I can use Z/E with all alkenes that have a stereogenic center

Z: the bigger 2 groups together.

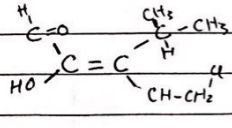
E: the bigger 2 groups opposing each other.

* نفس الطريقة في التحديد (نفس الاولويات)

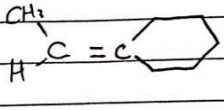
• 

high

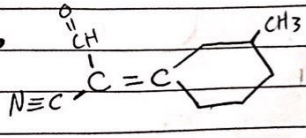
Z

• 

E

• 

not a stereogenic Center

• 

Z

الـ E, Z تنزل في السنة

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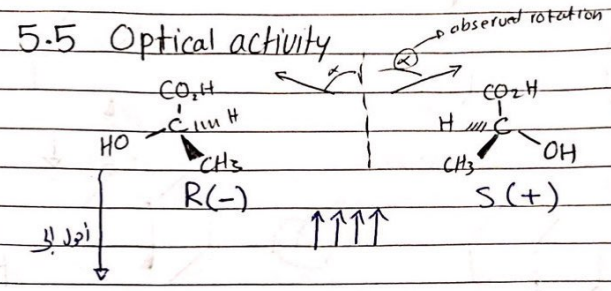
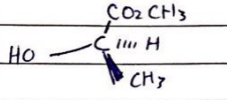
No.

5.5 Optical activity





R(+)

في أن +، − لا علاقة لها بـ R, S

* Observed rotation is measured by polarizometer, it changes with wave lenght & conc.

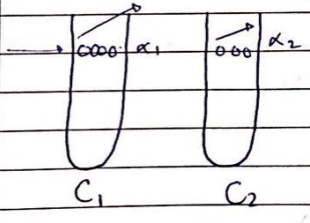
$[\alpha]^{\lambda}_{T}$ — λ → wave lenght ثابت
— T → Temp ثابت (25°)

$$[\alpha]^{\lambda}_{T} = \frac{\alpha}{C \cdot L}$$

l : length (dm)

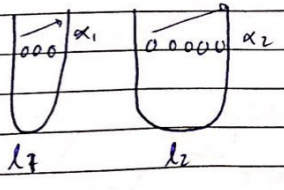
C : concentration (g/cm^3)

→ specific rotation (constant for each compound)



*عندما يزداد التركيز يزداد عدد الجزيئات التي سيصطدم بها الضوء فيزداد الانحراف.

• $C_1 > C_2$



• $l_2 > l_1$ • $\alpha_1 < \alpha_2$

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5

No.

* Solve problem 30 in the book.

* If C x 10 ⟶ observed rotation increases by 10.

- eg: $[\alpha] = +86.6°$ For S
  for R which is diluted 10 times
- constant → S.R = $-26.6°$
- might change → O.R ⟶ يزيد بزيادة conc ويقل بنقص الـ conc.

Scanned by CamScanner

Scanned with CamScanner

No.

* Solve problem 30 in the book.

* If C x 10 ⟶ observed rotation increases by 10.
  - eg: $[\alpha] = +86.6°$ For S
    for R which is diluted 10 times
  - constant → S.R = $-26.6°$
  - might change → O.R ⟶ conc يزيد بزيادة conc وقل بنقص ال

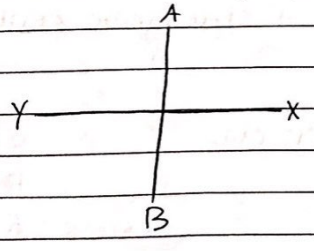
α : observed rotation (varied) ⟶ (+)R (−) S
+ 28.7° −28.7°

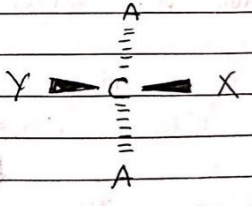
$[\alpha]_T^{\lambda}$: specific rotation (constant) ⟶ −10.17°

* Racenic mixture is (1:1) mixture of the two enantioners which is optically inactive.
  A-Chiral racenic mixture } ⟶ optically inactive

* We have S ⟶ asked for R considering it's diluted (10 times less) then:
  O.R is 10 times less & of coure opposite (+ ⟶ −) (− ⟶ +)

5.7 Fisher projection:





- horizintal ⟶ للعين
- vertical ⟶ داخلين

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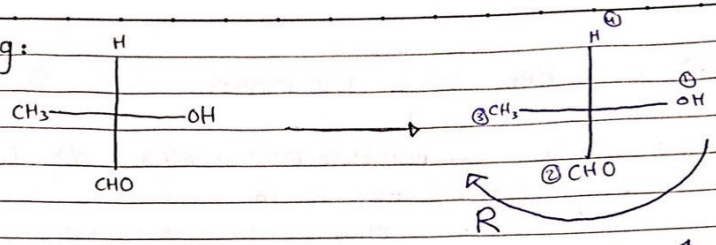
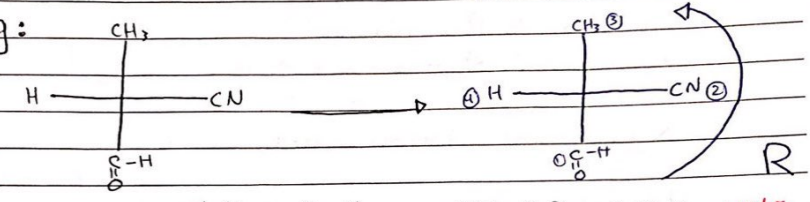
No.

eg:



eg:



Notes: * إذا المجموعة 4 داخلة ⟵ نفس ال rotation.

* إذا المجموعة 4 خارجة ⟵ عكس ال rotation.

5.8 Compounds with more than One chirality Centers :

eg: $CH_3-\overset{Cl}{\underset{*}{\overset{|}{C}}}H-\overset{Br}{\underset{*}{\overset{|}{C}}}H-CH_3$

S	S
R	S
S	R
R	R

احتمالاتهم :
- 4 sets of configuration
- each one represent stereoisomers
- 4 stereoisomers

$2^2 = 4$

2^n = total number of stereoisomeres
where n is total number of stereogenic centers

eg: $CH_3\overset{OH}{\overset{|}{C}}H-CH=CH-\overset{CH_3}{\overset{|}{C}}-CH_2CH_3$

↓

$CH_3\overset{OH}{\underset{*}{\overset{|}{C}}}H-CH=CH-\overset{CH_3}{\overset{|}{C}}-CH_2CH_3$

S cis S	S trans S
S cis R	S trans R
R cis S	R trans S
R cis R	R trans R

$2^3 = 8$ stereoisomeres

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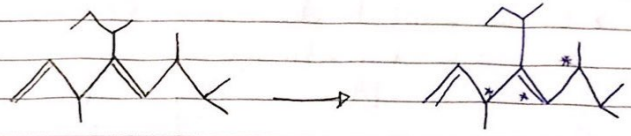
Scanned with CamScanner

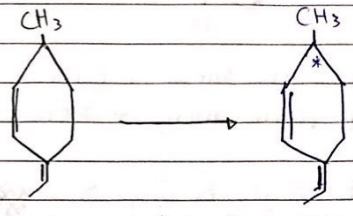
No.

eg:



$2^4 = 16$

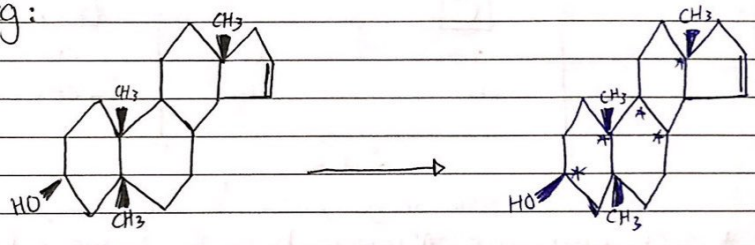
eg:



$2^2 = 4$

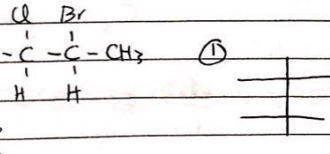
- * → inside cycle is not a Chirality Center

eg:



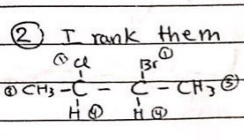
$2^7 = 128$

* In exam: How many stereogenic Centers?



①

② I rank them



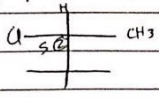
S - S

R S

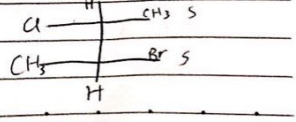
S R

R R

③ 4 → داخله



④ أضع ① و ② بيشكون S أو R حسب الطلوب



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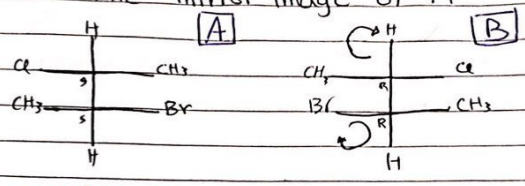
No.

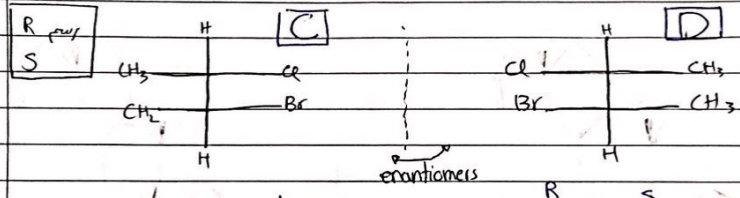
* If we want to draw R R from S S we just draw the mirror image of it



enantiomers

* enantiomers → mirror image + Chiral
→ mirror image + stereoisomeres

*إذا كل ال S صارت R وكل ال R صارت S إذا هم enatiomeres
(حتى إذا لم أستطع رؤية هم كـ mirror image لبعضهم)



*لرسم R S من R S نستخدم Mirror image

* each pair of enantiomers have the same color, solubility, boiling point, melting point → but ... different in Optical activity.

*مرئيًا" إذا واحد ثبت والثاني انعكس تسمى diastereomers
مثل A مع C او D مع B أو C مع D
→ stereoisomes, but NOT mirror image.

*أجرب التمييز بصريا" إذا لم أتمكن من ذلك أذهب إلى ال Config.

*إذا واحد منهم ال config ثبت والثاني انعكس إذا هم diastereomers

* diastereomers are different compounds → different Colors, boiling points → optically active but have different α.

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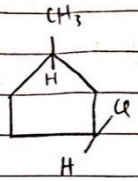
5

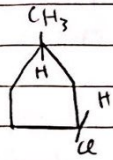
cis/trans → diastereoisomers

No.

eg:



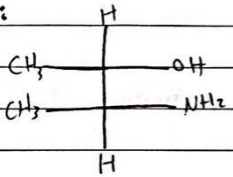
Cis

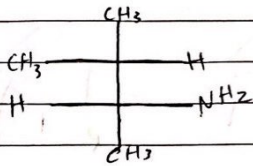


trans

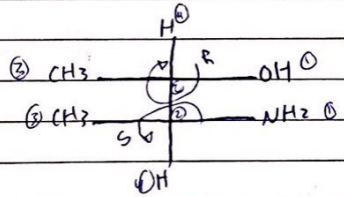
diastereoisomers

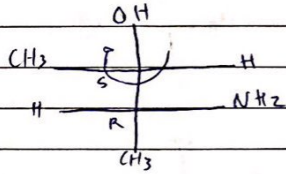
eg:





* steps to solve such questions:
  1. are they mirror image?
  2. did one stay & the other change?
  3. Config.





enantiomers (& conformers

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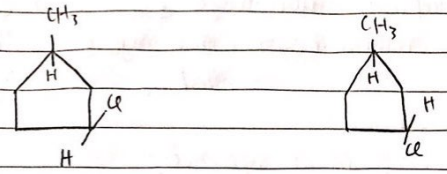
5

cis/trans → diastereoisomers

No.

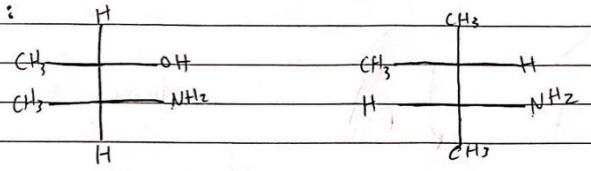
eg:



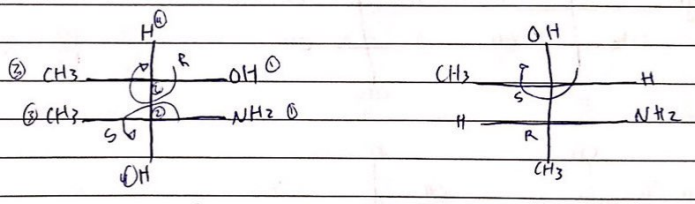
Cis trans

diastereoisomers

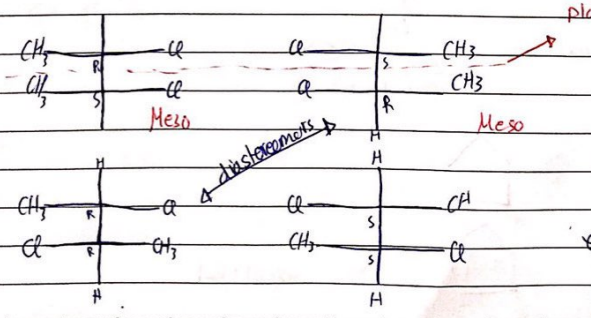
eg:



* steps to solve such questions:
  1. are they mirror image?
  2. did one stay & the other change?
  3. Config.



enantiomers (N conformers



plain of symmetry
both A-Chiral
identical

enantiomers

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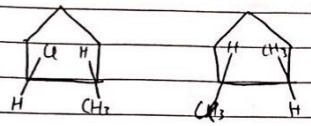
No.

* إذا مركب Meso ← mirror image يكون identical.
* Chiral ← mirror image يكون enantiomer مختلف في O.A
* إذا لم يكن Meso فهو Chiral.

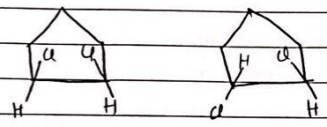
- How to know it's Meso?
1) If there is plain of symmetry
2) If the 2 chirality centers are connected to the same group & one is R & the other is S.

eg.



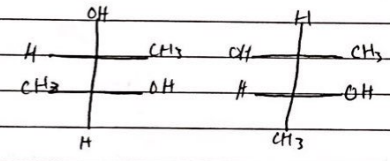
enatiomes

eg.

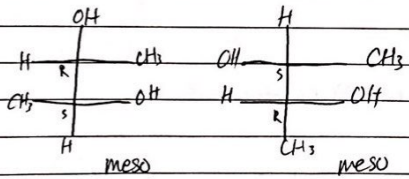


diastereomers

eg.

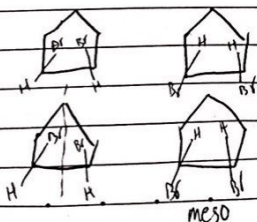


eg.



meso meso
identical

eg.



identical

meso meso

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5

Linalool → stereospecific

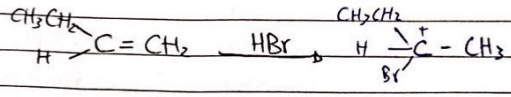
No.

5.11 Stereochemistry & Chemical reactions

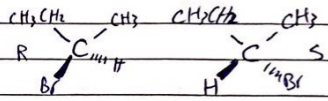
*If there is a rxn that gives stereoisomers & gives one of the options more than the other.

- Stereoselective → يعطي واحد أكثر من الآخر
- non-stereoselective → بنفس الكمية

*Electrophilic addition as an example:



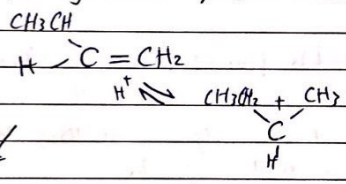
A-Chiral



50% 50%

racemic mixture

*If we start with A-Chiral Alkene it gives racemic mixture (optically inactive) (not stereoselective)

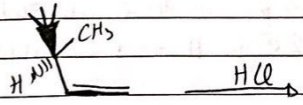


نوع التهجين sp^2 → planar → فرصة الهجوم من جهتين متساوية

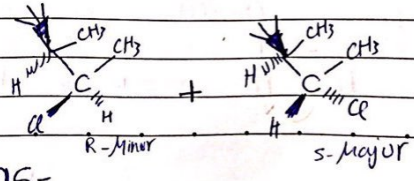
$\boxed{\text{تكون Carbocation كـ intermediate يعني أن التفاعل non-selective}}$

* الـ carbocation شكلها planar تسهل الهجوم.

eg.



Chiral (S)



*tetra-butyl تسوي إضافة

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6 × 5

No.

* If we start with Chiral we end up with a mixture of diastereomers (Major & Minor)

~~5.12~~

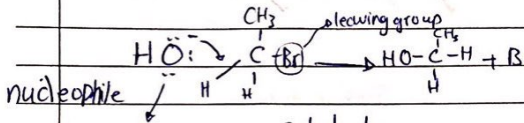
CH.6 Substitution & Elimination

$$:\ddot{O}H^{\ominus} + CH_3CH_2Br \longrightarrow CH_3\overset{OH}{C}H_2 + CH_2=CH_2$$

substitution — elimination

↓

H & Br are removed & replaced with a =



has lone pairs of e^-

↓

OH attacks the Carbon connected to Br

↓

OH^- starts to donate the lone pair of e^- to the carbon

↓

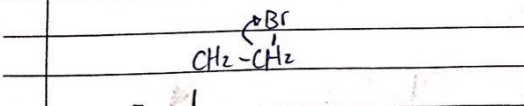
Br leaves

* Substitution happens on many compounds including alkyl halide
* neucleophile : The One that gives $2e^-$.
* leaving group : Stable
* Substrate : What is Substituted (for us it will be alkyl halide)
* OH^- acts as a base → give e^- to H that leaves as H^+

↳ has double behavior

↳ neucleophile when donates $2e^-$ to C → subs

↳ base when donates $2e^-$ to H → elimination



$$HO^{-}: H \longrightarrow CH_2=CH_2 + H_2O + Br^-$$

elimination

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6

No.

* you have to know nucleophiles → primary, secondary, tertiary

Nucleophiles :

Ionic		Neutral
OH^-		H_2O
HS^-	Sulfide	H_2S
NH_2^-	amide	NH_3
CH_3O^-	alkyl oxide	CH_3OH
CH_3S^-	alkyl sulfide	CH_3SH
CN^-		
F^-		
Cl^-		
Br^-		
I^-		
CH_3NH^-		$CH_3\ddot{N}H_2$

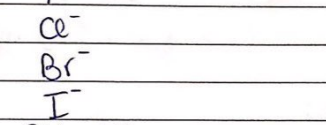
* ionic nucleophile are stronger than neutral

معلومات حسب قوة النوكليوفيل وحسب نوعية الـ alkyl halide

6.4 SN^2 mechanism reaction (mechanism for substitution)

$$H\ddot{S}^{-1} + CH_3\overset{Br}{C}H_2 \longrightarrow CH_3\overset{SH}{C}H_2 + Br^-$$

(هذا التفاعل لا يكون في عين طبعي)



Primary

* primary alkyl halide

لا يحدث معه غير SN^2 reaction (100% SN^2)

* SN^2 happens in 2 notary

doesn't happen in tertiary

SN^2:

* Nucleophile from opposite direction of the leaving group (180° بين وبين الـ halide)
* One step reaction / transition state / with no intermediates

occurs via a

no carbocations / no carboanions

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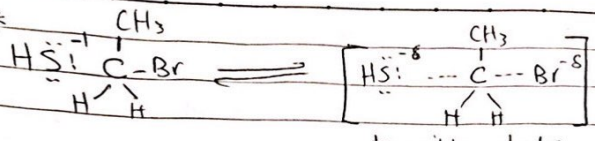
No.

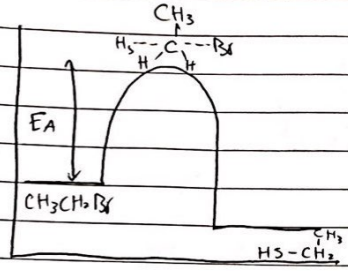
عكس دائماً" في الامتحان الرسمة *



transition state

* Nu و leaving group ⟶ 180° بينهم

* يجي من الجهة المعاكسة ⟵ يفرغ النوع الالكتروني ⟵ تزال ال leaving group



EA S_N^2 very high

* الكربونة في ال transition state حولها 5
↓
التنافر عالي
↓
الطاقة عالية
↓
Ea is very high

rate $SN^2 \propto [Nu][sub]$ sub: substrate

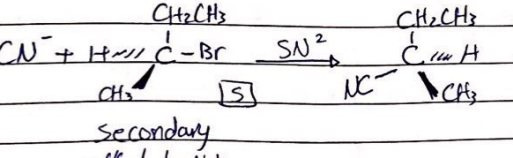
rate $SN^2 = K [Nu]^1 [Sub]^1$

order = مجموع الـ powers = 2

S substitution / N nucleophilic / 2 second order

* إذا كان secondary alkyl halide ⟵ نشال عن Nu ⟵ وتحتاج strong Nu
حتى يكون SN^2 لأن SN^2
هجوم مباشر

* The rate of the reaction depends on both the conc. of Nu & substrate.



secondary alkyl halide

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No.

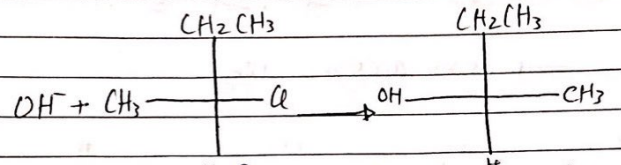
* strong Nu → ionic + Sulfur containing

SN^2 ← primary * أمينات

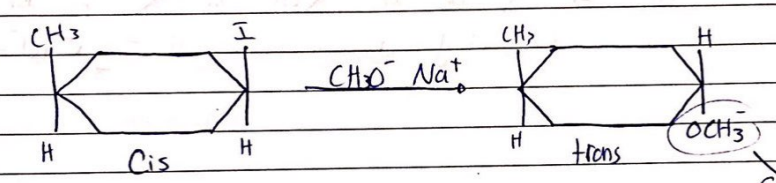
leaving group is on achiral

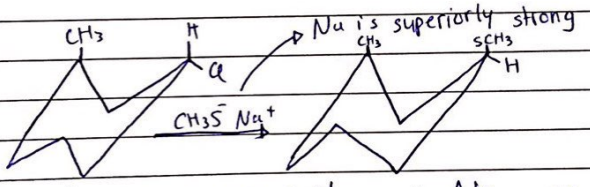
* SN^2 reaction is associated with inversion in the chirality of compound from S to R & from R to S

لأن Na يأتي من الجهة المعاكسة لل leaving group



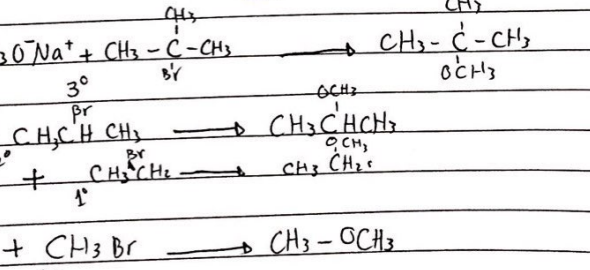
* الارتباط يحدث من خلال ذرة hetero atom وليس الكربون.





* leaving group axil → Nu eq والعكس

* كلما كان Nu أقوى ← التفاعل أسرع



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No.

* strong Nu ← has high e^- density ← تنافر عالي على الذرة المانحة
← استقرارية أقل ← يسعى للاستقرار ← يمنح $2e^-$.

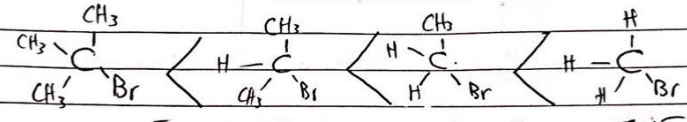
reactivity (SN^2) أسرع

$$\underset{\text{tert}}{3^\circ} < 2^\circ < 1^\circ < \text{Methyl}$$

SN^2 reaction never occurs with tert (No subs → only elimination)

* السبب في الترتيب هو أن التفاعل direct attack ← needs more access

وهكذا ← less access ← عند إضافة مجموعات كبيرة (يعني primary, sec)



* كلما كبرت المجموعات ← قل السرعة.

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Things that seem to not make sense here : ① + ②

No.

* Strong Nu ← has high e^- density ← تتواجد على الذرة الحاملة
← استقرارية أقل ← يعني للاستقرار ← يطلق $2e^-$.

reactivity (SN^2) أسرع

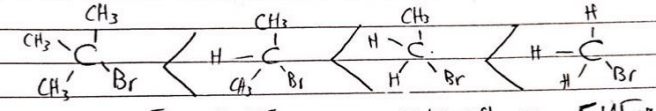
$$\underset{\text{أبطأ}}{3^\circ} < 2^\circ < 1^\circ < \text{Methyl}$$

SN^2 reaction never occurs with tert (No subs → only elimination)

* السبب في الترتيب هو أن التفاعل direct attack ← needs more access

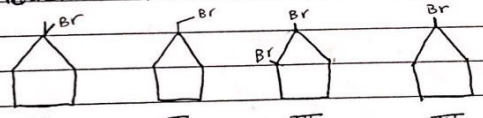
↓

وهكذا less access ← عند إضافة مجموعات كبيرة (وفي الـ Primary)



* كلما كبرت المجموعات ← تقل السرعة.

* Rank the following alkyl halides according to their reactivites toward nucleophilic substitution reaction by HS^{-1} (superorly strong)

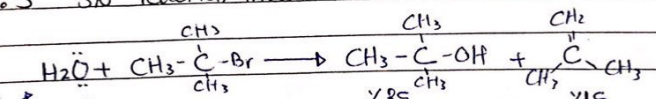


I II III IV

Sol: 3° 1° 2° 2°

II > IV > III > I

6.5 SN' reaction mechanism:



① weak Nu

② How did it react with 3° (high steric strain) ?

↓

الحل: لازم تنكسر الرابطة بين C و Br ← تكوين Carbocation

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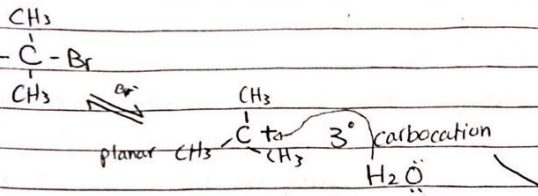
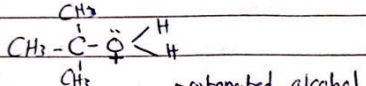
No.



انحلت مشكلة 1

* يجذب أي Nü مهما كان ضعيف حيث أن الـ C.C جذاب حتى لا ضعف Nü

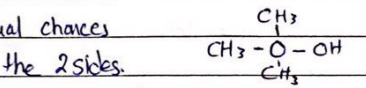
* الـ $H_2\ddot{O}$ neutral (لذلك ضعيف) ← عندما يهجم يطلع +



ص. بالنار

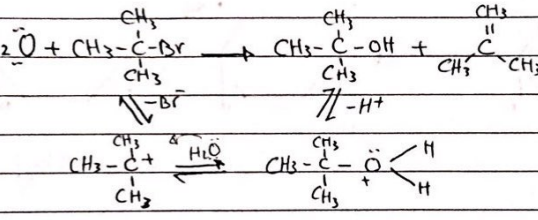
protonated alcohol (pronated ether, ------)

$-H^+$



* الـ C.C هو sp^2 ← (انحلت مشكلة ②)

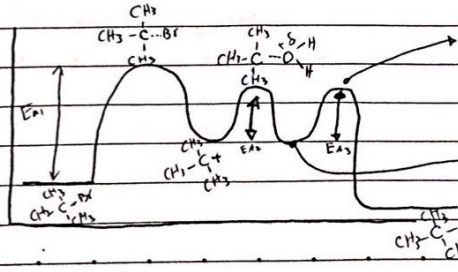
(راح الـ - sterich)



SN1: strong Nü → attack / elimination → يستقر بأي طريقة ولا ينتظر C.C

weak Nü → ينتظر

* Formation of C.C is the slow rate determinating step



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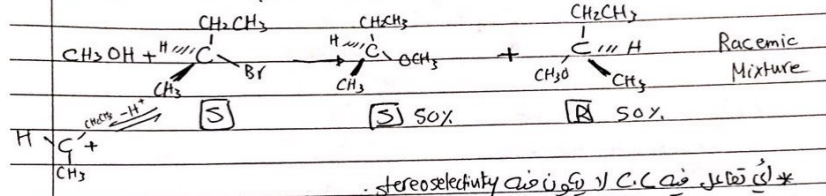
*كل التفاعلات اللي فيها intermediate C.C
← تكون سرعتها معتمدة على مدى استقرار

No.

* E_{A1} هو الأعلى
* rate of $SN^1 \propto [sub]$
* Nu conc / strenght has nothing to do with the rate
→ rate of $SN^1 = K[sub]^1$ first order
• rate of reaction depends only on the conc of the substute → alkyl halide.

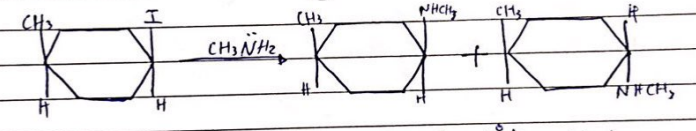
Stereochemistry of SN^1



* أي تفاعل فيه C.C لا يكون فيه stereoselectivity.

* SN^1 reactions lead to forming racemic mixture (1:1 / S, R)

eg.



eg.

$3^\circ > 2^\circ > 1^\circ >$ methyl

$CH_3OH + CH_3-\overset{3^\circ}{C}(CH_3)_2-Cl$ (weak Nu)

$CH_3-C(Cl)(CH_3)-CH_3$

$[CH_3-CH_2]$ لا يحدث فيها SN^1 لأن ICC غير موجود فيها

$[CH_3Cl]$ لا يحدث فيها

$^\circ 2$ alkyl halide → strong Nu → SN^2
→ weak Nu → SN^1

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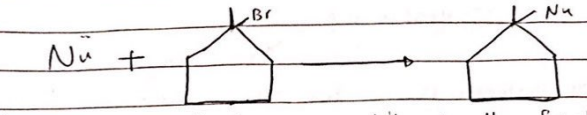
No.

eg. As in the following reaction:



* Which of the following nucleophiles is the fastest?

CH_3OH $CH_3O^-Na^+$ $CH_3\bar{N}H_2$ H_2O NH_3

Solu: all are the same

Nucleophile:

1. Ionic Nucleophiles are stronger than neutral nucleophiles

$NH_2^- > NH_3$ $HS^- > H_2S$

$CH_3O^- > CH_3OH$ $OH^- > H_2O$

2. nucleophiles with less electronegative donating atoms are stronger than nucleophiles with more electronegative atoms

* عدد الأزواج الالكترونية لا علاقة له بقوة Nu

$H_2\ddot{O} < H_2\ddot{S}$ * العامل الأيوني أقوى من عامل الكهروسالبية

↓ less E.N

↓ giving away $2e^-$ becomes easier

eg. $\bar{C}H_3^-$ / $:\bar{N}H_2^-$ / $:\ddot{O}H^-$ / $:\ddot{F}:^-$

$CH_3^- > NH_2^- > OH^- > F^-$

أضعف

أقوى

$I^- > Br^- > Cl^- > F^-$

Solvent:

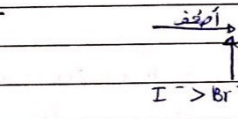
* يفصل الـ ions عن C.C (يعمل مثل عمل H_2O , NaCl)

* SN^1 & SN^2 both require polar solvents

* لأنه في كلا التفاعلين لازم تنكسر الرابطة بين الـ leaving group والـ C

- $-\overset{|}{C}-L$
- $Nu \rightarrow -\overset{|}{C}^{\delta+}-Cl^{\delta-} \rightleftharpoons -\overset{|}{C}^{+} + Cl$
- $-\overset{|}{C}^{\delta+}-Br^{\delta-} \rightleftharpoons -\overset{|}{C}^{+} + Br^-$
- $-\overset{|}{C}^{\delta+}-I^{\delta-}$
- $-\overset{|}{C}^{+\delta}-F^{-\delta}$

$NaCl \rightarrow Na^+ + Cl^-$



solvation

solvent molecules surrounding solute ions separating them

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No.

Solvation of Nü ← SN^2 الـ في حالة *

Solvation of substrate ← SN^1

↳ Alkyl halide

* all polar solvents work for SN^1.

* SN^2 require polar & a protic solvent.

$H_2O \rightleftharpoons H^+ + OH^-$

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

$CH_3\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-O^- + H^+$

} Protic يعطي H^+

* a protic

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ aceton

$CH_3-\overset{O}{\overset{\|}{S}}-CH_3$ dimethylsulfoxide "DMSO"

$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$ Dimethylformamide "DMF"

* polar protic diminish the rate of SN^2 reaction

يثبط

$H\ddot{O}:^- + CH_3OH \rightleftharpoons CH_3O^- + H_2O$

strong Nü → weak Nü

يقلل تركيز الـ N القوي في الـ sol

eg. Which of the following increase / diminish the rate of reaction

A) B) C) D)

6.7 Elimination reactions:

$CH_3O^-Na^+ + CH_3CH_2\overset{Br}{\overset{|}{C}}H_2 \longrightarrow CH_3CH_2\overset{OCH_3}{\overset{|}{C}}H_2 + CH_3CH=CH_2$

1° ٪65 ٪35

Major product الـ ← SN^2 E_2

* SN^2 يحدث معها E_2 فقط.

* SN^1 يحدث معها E_1 فقط.

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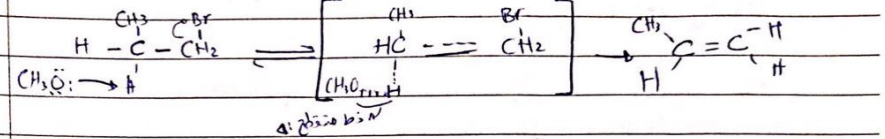
No.

* الـ E_2 مثل SN^2 ولكن بدل من Sub يكون elim
* يجب أن يكون على الكربون (المجاورة للكربون اللي عليها Br) عليها H

$CH_3-CH_2-\overset{Br}{CH_2}$

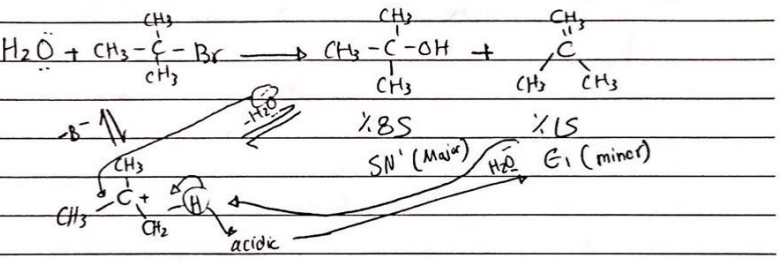
* في نفس الوقت تنكسر الروابط وتكون Pi وتغادر الـ leaving group.
* هل هاذا نعتمد السرعة / هاذا ينبع ← مثل SN^2



ذا منتقل :

* One step / one transition state / no intermediates

* مع الـ weak Nu في SN^1 و E^1 والـ Major هو SN^1



* أول شي يتكون الـ C.C ثم تسحب H من المجاورات وبما أن H very acidic حتى الضعيف يسحبها Nu

* SN^1 reaction is faster than E_1 due to lower activation energy.

(No bond breaking just nucleophilic attack) (يحتاج لكسر رابطة H-C وهذا يحتاج طاقة)

Weak Nu + 2°/3° → Major SN^1 + Minor E_1

* Alkenes that has more substitutions are more stable.

$CH_3O^-Na^+ + CH_3CH_2\overset{Br}{C}HCH_3 \longrightarrow CH_3CH_2\overset{OCH_3}{C}HCH_3 + CH_3CH=CHCH_3$

unstable → needs to be stable fastly

minor SN^2 — major E_2

in 1° → a lot of open space → easy access → SN^2 major

2° → less space → harder to attack

3° → hard to attack → %100 E_2

harder to attack ~ more attack on H → SN^2 minor.

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No.

$$CH_3O^-Na^+ + CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-Br \longrightarrow \overset{CH_3}{\overset{\|}{C}}(CH_3)_2$$

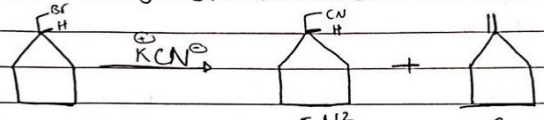
3° ×100 E_2

Strong Nu^- + °1 → SN^2 major + E_2 minor
strong Nu^- + °2 → SN^2 minor + E_2 major
strong Nu^- + °3 → ×100 E_2

6.8 Substitution & Elimination competitions

[1] Primary alkylhalide

Major SN^2 / Minor E_2

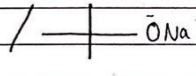


major SN^2 minor E_2

$$CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}H + CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O^-Na^+ \longrightarrow \text{strong base / weak } Nu^-$$

$$\longrightarrow CH_3CH_2CH_2CH_2-O-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 \quad \text{minor}$$

$$+ \; CH_3CH_2CH=CH_2 \quad \text{major}$$

$(CH_3)_3CO^-Na^+$ /  $\bar{O}Na^+$ / $\bar{O}Na^+$

[2] tertiary alkyl halide

(A) Weak Nu^- → SN^1 major

CH_3OH +

major SN_1 minor E_1

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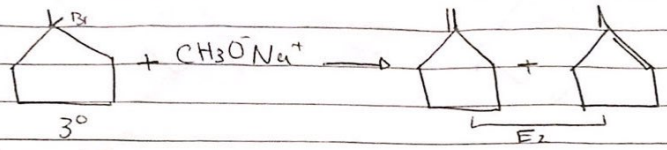
No.

(b) strong Nu [E2 only]

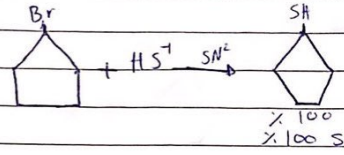


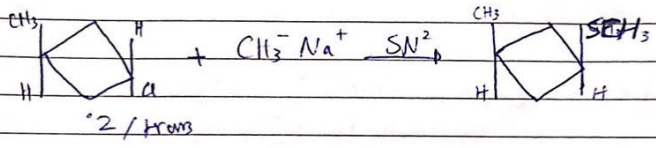
(c) Secondary

① with sulfur - containing nucleophile

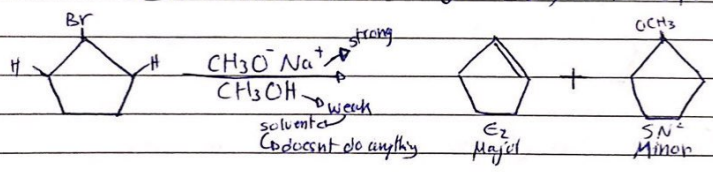
superiorly strong Nu

sub %100





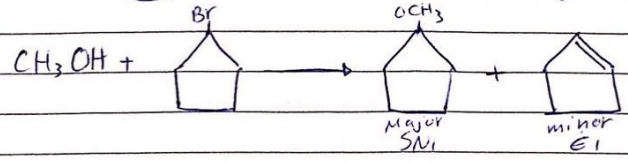
② with ionic Nu (Major E2 , minor SN2)



* alkoxides : ($CH_3O^-Na^+/CH_3OH$) يتفاعل SN^2

لما هيئ الكحولات يتم تحضيرها بإضافة بدل
الى الكحول لانه دائماً حجم المركب مع الكحول

③ with weak Nu (SN1 major , E1 minor)



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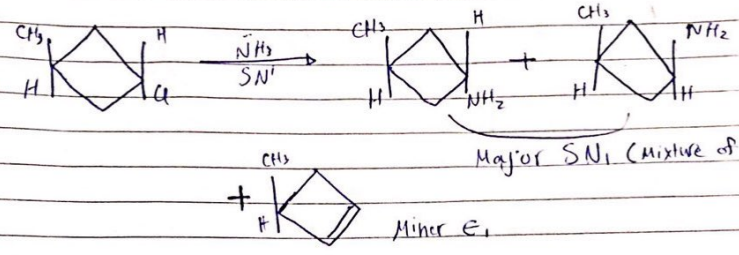
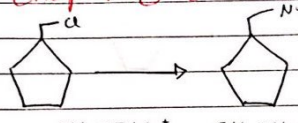
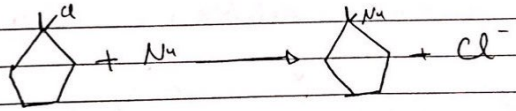


Examples of N chapter 6 :

eg. Nu + 

CH_3OH CH_3NH_2 $CH_3O^-Na^+$ CH_3CH_2OH all are the same

Sol : (1° alkyl halid ال)) SN2 لان التفاعل
We look for the strongest Nu
$CH_3O^-Na^+$



* نفس الدولار

Sol : SN1 (3° ال) → all are the same
(substrate ال لانه يعتمد على).

End of Chapter 6 El-Zeen :)
Enjoy people
Good luck

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No.

CH 7 : Al-cohols & Phenols

مشتركين في خاصيه hydrogen bonding ومختلفين في باقي الصفات

Functional group (-OH)

* Phenols ⟶ its Chemistry is aromatic
* any compound has OH & no carbonel ($\overset{O}{\overset{\|}{C}}$) group is an alcohol ⟶ Name has -ol

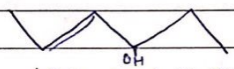
• $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2CH_2CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

6-Methyl-2-octanol — * least possible # for (ol)

• $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$

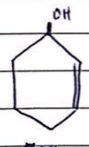
3-methyl-2,5-heptanediol — * If I have 2 (OH) I call it diol

•

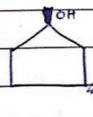


trans-hex-4-en-3-ol

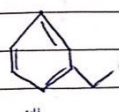
The book ← trans-4-hexen-3-ol

• 

2-cyclohexenol — * in cyclic compounds If I have one OH then by default it holds # one

• 

trans-3-aminocyclopentanol

• 

benzylalcohol, phenylmethanol (common name)

•

p-methyl Phenol
4-methyl Phenol

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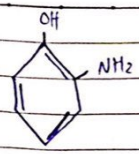
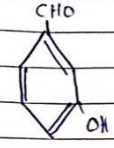
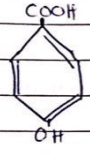
- 

2-aminophenol
O-aminophenol

- 

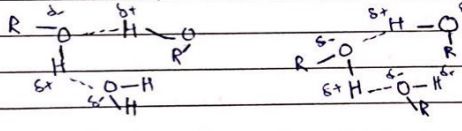
3-hydroxybenzaldehyde

- 

4-hydroxybenzoicacid

7.4 Physical properties of alcohols:

* all these physical properties are due to hydrogen bonding between itself & with water.



① alcohols have high boiling points due to hydrogen bonding intermolecular forces

② They have high solubility in water due to hydrogen bonding interaction that alcohol molecules can make water molecules

* more OH groups ⟶ higher boiling points

$CH_3\ CH_2\ CH_2\ CH_2$ — 117°C, OH

$CH_2\ CH_2$ — OH, OH — 205°C

* Solubility ⟶ more C atoms ⟶ less soluble in water

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7

No.

CH_3OH CH_3CH_2OH $CH_3CH_2CH_2OH$

Miscible in water (one layer)

$CH_3CH_2CH_2CH_2OH$

18 g/100 ml H_2O

* ابتداء من الكربونة الرابعة تبدأ الـ solubility تقل

R – OH → polar hydrophilic

يتجاذب مع الماء

hydrocarbonic
non-polar
hydrophobic

Vander Vall forces

لا تجذب الماء

The longer the C chain the more Vander Valls forces & the more the alcohol gets attached to other molecules of itself & leave water

* more branching → more soluble in water

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7

* acid = proton donor

No.

CH_3OH CH_3CH_2OH $CH_3CH_2CH_2OH$

Miscible in water (one layer)

$CH_3CH_2CH_2CH_2OH$

18 g/100 ml H_2O

* ابتداء من الكربونة الرابعة تبدأ الـ solubility تقل

R – OH → polar hydrophilic

يتجاذب مع الماء

hydrocarbonic
non-polar
hydrophobic

Vander Vall forces

لا تحب الماء

The longer the C chain the more Vander Valls forces & the more the alcohol gets attached to other molecules of itself & leave water

* more branching → more soluble in water

7.5 acidity of alcohols & Phends

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

acid — conjugate base

acid — conj. base

if this is strong $\xrightarrow{\text{then this}}$ weak

weak → strong

weak acid → Partial dissociation → we have equilbrium

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

usually used to see if the acid is strong or not but we will be using PKa as a strenght indicator.

Ka	PKa	
10^{-3}	3	strong
10^{-10}	10	weak

Ka قليلة → $[H^+]$ قليل → حمض أضعف

Ka عالية → $[H^+]$ أعلى → حمض أقوى

[* stronger acid = lower PKa Value]

* If I wanted to explain why an acid is strong/weak then I go to the conjugate base & analyse it.

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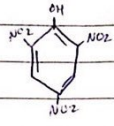
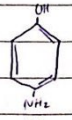
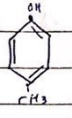
No.

* Stronger base has higher e^- density at the donating atom.
* stronger base has Less E.N donating atom

* كثافة الكترونية عالية في ال base ← تنافر عالي ← سهولة أكبر في إعطاء e^- ← كلما زادت هذه السهولة زادت قوة القاعدة.

* Lewis base : lone pair donor

* الكثافة على ال Base قليلة ← تنافر قليل ← منح $2e^-$ أصعب ← قاعدة أضعف

Compound	PKa	compound	PKa
H_2O	15.7		0.23
CH_3OH	15.5		
CH_3CH_2OH	15.9		
$(CH_3)_3COH$	18.0		
F_3CCH_2OH	12.3		10.7
	10		
	9.3		10.3
	7.2		

* Alcohols are weak acids same as water
* Phenols are stronger as acid then alcohols

* Acidity of alcohols : methanol > 1° > 2° > 3°

(مجموعات زادت — مجموعات 3)

* كلما زادت المجموعات الدافعة على الكحول نصبح القاعدة أقوى أي الحمض أضعف

• $(CH_3)_3COH \rightleftharpoons H^+ + (CH_3)_3C-O^-$ → high electron density → higher repulsive interactions → easier to give up lone pair of e^- → stronge base → weakes acid.

* in methanol we don't have e^- decreasing group.

* $CH_3CH_2OH \rightleftharpoons H^+ + CH_3CH_2O^-$

• $F_3CCH_2OH \rightleftharpoons H^+ + F_3C-CH_2-O^-$

* كلما كانت المجموعة الساحبة أقوى ← stronger acid
* وجود مجموعات ساحبة على الكحول تعطي قاعدة أضعف / حمض أقوى
* كلما زاد عدد المجموعات الساحبة ← stronger acid

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conjugate base of alcohol = alkyl oxide

No.

eg. Rank the following alcohols according to their acidities.

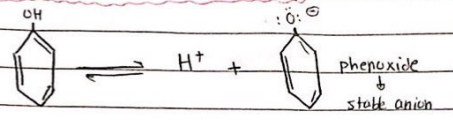
- CH_3OH ICH_2OH $BrCH_2OH$ $ClCH_2OH$ FCH_2OH

Sol: $CH_3OH < ICH_2OH < BrCH_2OH < ClCH_2OH < FCH_2OH$

- $ClCH_2OH$ FCH_2OH F_2CHOH F_3COH

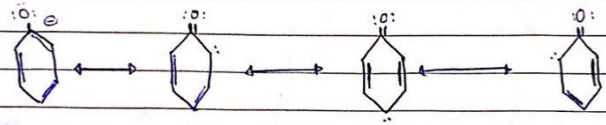
Sol: $ClCH_2OH < FCH_2OH < F_2CHOH < F_3COH$

* Now we'll discuss Phends:



* When a compound is more stable in an equilibrium than other compound in this equ → this cause shifting in eq.

* Phenoxide: stable due to reasonance structure.

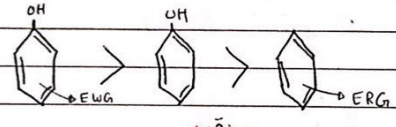


ممكن التفسير بطريقتين: ① phenoxide more stable → eq shifted to the right → more H^+ is given → stronger acid.

② electron density on oxygen of phenoxide is not localized (delocalized) → less e.d on O → harder to donate $2e^-$ → weaker base → phenol is stronger acid

($2e^-$ مشتركة بين O و 3 كربونات)

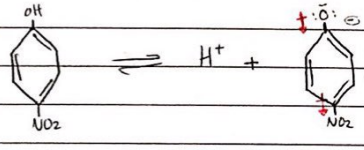
* Acidity:

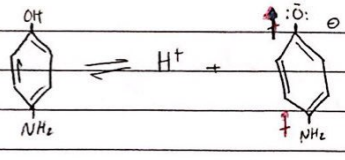


(1) Inductive effect → ناتج عن الشحنات (سالبة/موجبة)

(2) Reasonance effect

EWG





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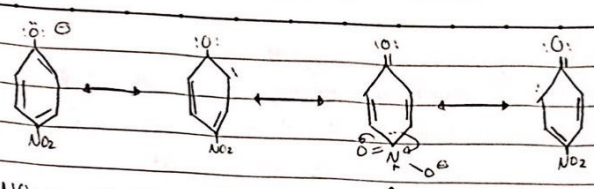
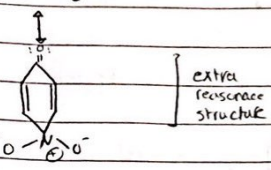


* NO_2 on ortha/para can draw an extra reasonance structure

↓ more stable

↓ more shifting in eq

↓ more H^+ → stronger acid

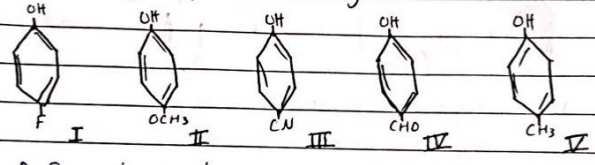


* ortho > para → لأنه اقربت الجهة

↓ stronger acid

more enductive effect الساحبة

eg. Rank the following compounds according to their acidities

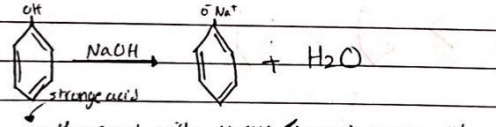


* strenge D.G → stronger acid

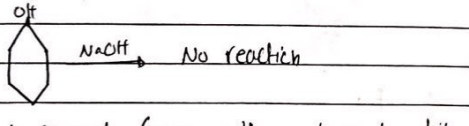
* stronger A.G → weaker acid

Sol: I De / II Ac / III De / IV De / V Ac

III > IV > I > V > II



so they react with NaOH (N even react with weaker base like bicarbonts)



- Very weak (even with a strong base like NaOH)
- NaOH can't deprotonate alcohols

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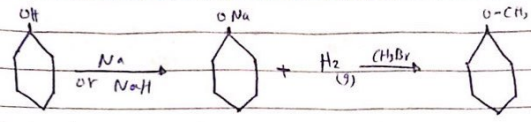
No.

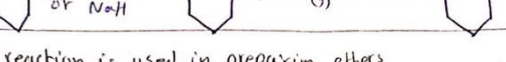
sodium hidride

* Na or NaH can deprotonate alcohols



* this reaction is used in preparing ethers
* alcohol is a weak Na so I need to deprotonate the alcohol first.

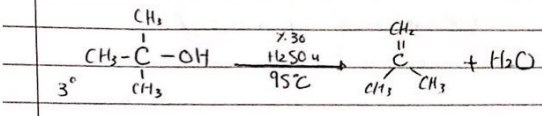
7.8 Dehydration of alcohols (نزع ماء)

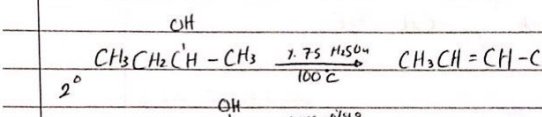


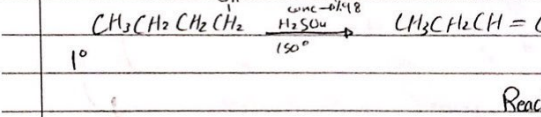
elimination of H_2O

* The reaction is acid-catalyzed / needs heat
* One carbon has OH & the neighbouring has H

• H^+: H_2SO_4, H_3PO_4







Reactivity: 3° > 2° > 1°

Results from the mechanism that the alcohol proceeds.

* The alcohol is ampholetic just like water
  • with acid → base (protonation for alcohol)
  • with base → acid
  * OH strong Na → bad leaving group
  * H_2O weak Na → good leaving group

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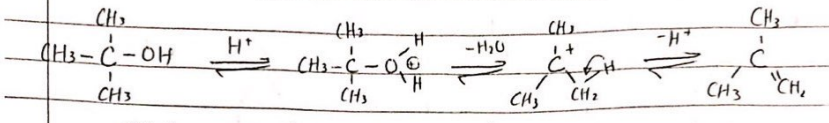
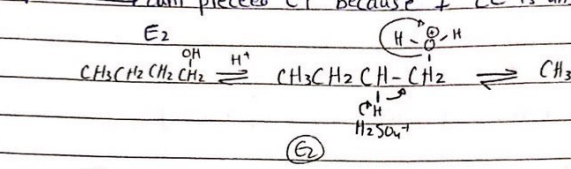
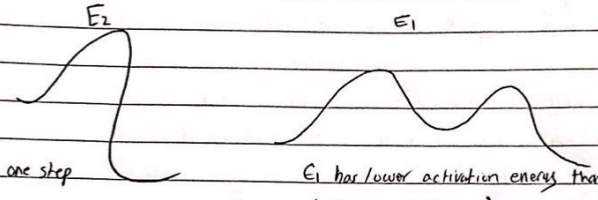


- 2°/3° ⟶ E1 (stable CC لانه بتكون)
- 1° ⟶ cant preceed E1 because 1° CC is unstable

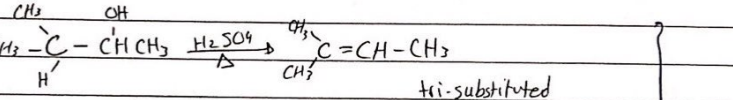




one step

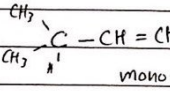
E1 has lower activation energy than E2
(3° more stable CC)

* Regoselectivity:



tri-substituted

Major / more stable

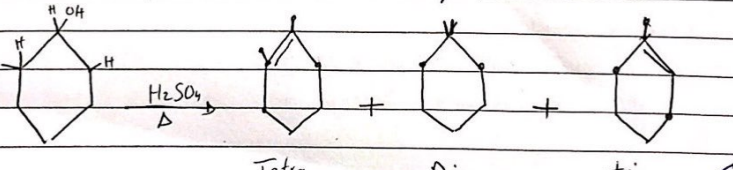


mono-sub minor

thermodynamic controlled reaction
always gives the more stable

* more sub alkene is more stabe

Tetra > tri > di > mono } stability of alkenes



Tetra Di tri E1

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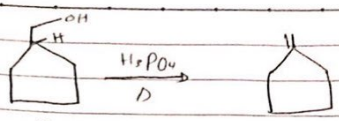
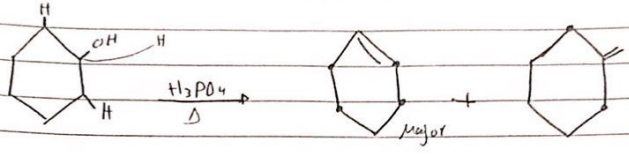


E_2



7.9 substitution of alcohols

$$-\overset{|}{C}-OH \xrightarrow{HX} -\overset{|}{C}-X + H_2O$$

HX = HCl, HBr, HI

- $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[\text{Room Temp (RT)}]{HCl} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + H_2O$
  15 min

- $CH_3CH_2\overset{OH}{C}HCH_3 \xrightarrow[\Delta]{HCl} CH_3CH_2\overset{Cl}{C}HCH_3 + H_2O$
  ½ hour

- $CH_3CH_2CH_2CH_2OH \xrightarrow[\Delta]{HCl}$ No reaction

*Reactivity of the reation: $\underbrace{3^\circ > 2^\circ}_{SN_1} > \underbrace{1^\circ}_{SN_2}$

*beca of formation of CC

*with primary, it depends on the acid used (which halogen which N.u)

- $CH_3CH_2CH_2CH_2OH \xrightarrow[\Delta]{HCl}$ No reaction
  HBr ↓ Δ ½ h

  $CH_3CH_2CH_2\overset{Br}{C}H_2$

3° • $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightleftharpoons{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{O}}^{\oplus} \xrightleftharpoons{-H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}^{\oplus} \xrightleftharpoons{Cl^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$

1° • $CH_3-CH_2CH_2\overset{OH}{C}H_2 \xrightleftharpoons{H^+} CH_3CH_2CH_2CH_2 \rightleftharpoons CH_3CH_2CH_2\overset{Br}{C}H_2$

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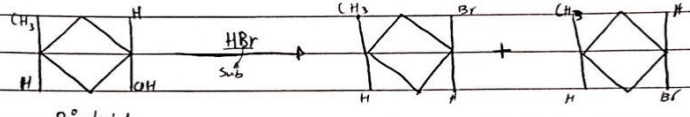
No.

- $CH_3CH_2CH_2CH_2OH \xrightarrow[\Delta]{HCl}$ No reaction

  $\xrightarrow{HBr,\ \Delta\ \frac{1}{2}h}$ $CH_3CH_2CH_2CH_2Br$

3°
- $CH_3-C(CH_3)_2-OH \xrightarrow{H^+} CH_3-C(CH_3)_2-O(H)_2^{\oplus} \xrightarrow{-H_2O} CH_3-C(CH_3)_2^{\oplus}$

1°
- $CH_3-CH_2CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2 \rightleftharpoons CH_3CH_2CH_2CH_2Br$

- 

  2° alcohol

أقوى EN يكون أسرع ← يعتمد على N4 ← SN^2 ← 1 alcohol

- $CH_3CH_2CH_2OH \xrightarrow{HX} CH_3CH_2CH_2X + H_2O$

  * HF HCl HBr HI All the Same] who is faster ?

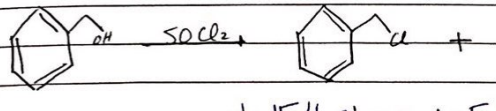
  - Solu: HI is faster

- $CH_3CH(OH)CH_3 \xrightarrow{HX} CH_3CH(X)CH_3 + H_2O$

  * HF HCl HBr HI All the Same] fastest ?

  - Solu: 2° alcohol → SN^1 → all the same

- $CH_3CH_2CH_2OH \xrightarrow[ZnCl_2]{HCl} CH_3CH_2CH_2Cl + H_2O$

- 

  $+ \underbrace{SO_2 + HCl}_{\text{advantage}}$

  غازية تطير

  * $SOCl_2$ يستبدل أي كحول ويحوله إلى كلورايد

  * $SOCl_2$ له limitations في الاستخدام

$SOCl_2$ Not used here

- $CH_3CH_2CH_2OH \xrightarrow{SOCl_2} \underbrace{CH_3CH_2CH_2Cl}_{\text{نحصل على كمية قليلة منه}} + SO_{2(g)} + HCl_{(g)}$

  has low boiling point

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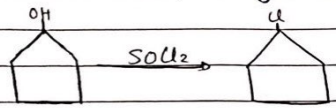
No.

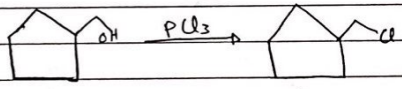
* $SOCl_2$ can't be used with alcohols that has low boiling points because it gives R-X with low boiling point that goes away with SO_2 & HCl gases.

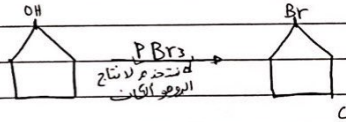


- $CH_3CH_2OH \xrightarrow{PCl_3} CH_3CH_2Cl + \underline{H_3PO_4}$

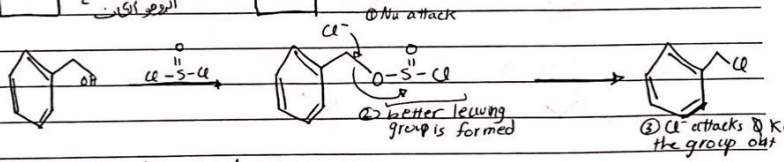
liquid / soluble in H_2O / high B.P

يتم الحصول على المركبات الناتجة نقي ماء هذوب H_3PO_4 بينما المركب الآخر non-polar لا يذوب فتنفصل عن بعضها.



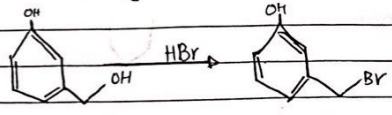


نستخدم لانتاج البروم الكاف



* $SOCl_2 / PCl_3 / PBr_3$

يتفاعلون SN^2 حتى مع ال 2°



7.12 Oxidation of alcohols

* signs of Oxidation:
  - more O around C
  - lower H around C

- more H / less O ⟶ reduction

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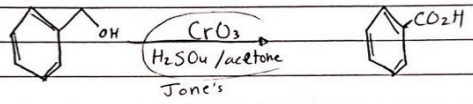
No.

1° • $CH_3\overset{OH}{\overset{|}{C}}H_2 \xrightarrow{[O]} \underset{\text{aldehyde}}{CH_3\overset{O}{\overset{\|}{C}}-H} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{CH_3\overset{O}{\overset{\|}{C}}-OH}$

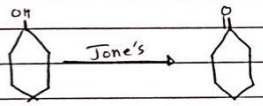
2° • $CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{[O]} \underset{\text{ketone}}{CH_3\overset{O}{\overset{\|}{C}}-CH_3}$

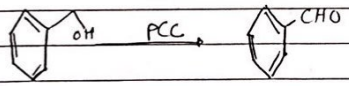
• $CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \longrightarrow$ No reaction

In° alcohol
- * Weak oxidation agent ⟶ stops at aldehyde
- * Strong Oxidation agent ⟶ continues to carboxylic acid

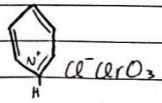
eg. 

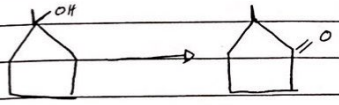
eg. $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Jone's}} CH_3CH_2CH_2CO_2H$

eg. 

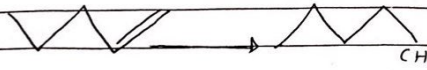
eg. 

eg. $CH_3CH_2CH_2CH_2OH \xrightarrow{PCC} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-H$

* PCC : Pyridinium chlorochromate 

eg. 

H.W :D

eg. 

H.W :D

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No.

7.13 Compounds with more than one hydroxyl group.

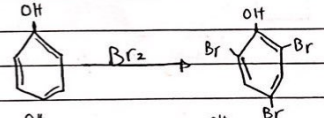
* these compounds in general are used for encapsulation (for drugs)

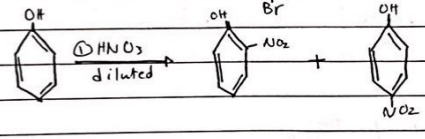
- $CH_2(OH)-CH_2(OH)$ Ethylen glycol
  ↳ used in antifreeze

- $CH_2(OH)\,CH(OH)\,CH_2(OH)$ Glysrol
  ↳ in making soap, beauty products
  ↳ as sugar for people with diabetes

- CH_2-ONO_2, $CH-ONO_2$, CH_2-ONO_2 } in explosives

7.14 Phenols ⟶ * Electrophilic aromatic sub
* extremely reactive

- 

- 

② T must be < 60°C ①+② conditions

* اذا ارتفعت الحرارة يصير عندي di/tri nitration

& this chapter is Clver if

BONNE CHANCE

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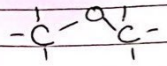
No.

CH. 8 ETHERS:

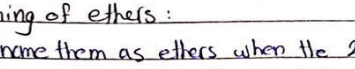


8.1 Naming of ethers:

* We name them as ethers when the 2 alkyl groups are kinda close to each other (small difference in # of C)

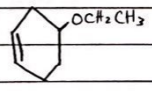
- $CH_3CH_2-O-CH_2CH_3$ — Diethyl ether
- $CH_3CH_2CH_2-O-CH_2CH_2CH_2CH_3$ — butyl propyl ether

* other than that its treated as a subs (alcoxy)

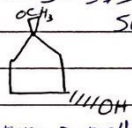


- 2-methoxypentane

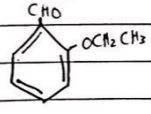
* بمجرد وجود مجموعة وظيفية واحدة في ال compound تتحول معهم ال ethers على أنه sub

eg. 

4-ethoxy cyclohexane

eg. 

trans-3-methoxy cyclopentanol

eg. 

- 2-ethexy benzaldehyde
- O- " " "

8.2 Physical properties

1 * Ethers have low boiling points same as alkanes

2 * Ethers have solubility in water same as alcohol

تقريباً نفس الكتلة

	$CH_3CH_2OCH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2OH$
B.P°C	38	36	117
Solubility in 100g water	8.3g	insoluble	7.8g

تقريباً

* أي مركب عضوي فيه Van der walls

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8

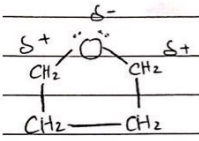
No.

A-cyclic ether $\overset{\delta+}{CH_3CH_2} - \overset{\delta-}{\ddot{O}} - \overset{\delta+}{CH_2CH_3}$ ⟵ Bent الروابط *
(مثل H_2O)

* dipole-dipole interactions is not effecient
(C-O is a polar bond)

because the hydrocarbonic wings shielded the polar bond which prevents dipole-dipole interactions.

cyclic ether

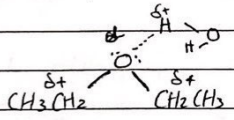


* the wing are tied back now ethers can form dipole-dipole interactions together

63°C

THF ⟵ اسم خاص له

* ethers are soluble in water because they have lone pair of e^- so they form hydrogen bonds with water + the water molecule is small & it can sneak in & form the hydrogen bonds.



* ethers are inert compounds they don't do these reactions:
~~oxidized~~, ~~reduced~~.

* At low pH ⟵ only case of reaction
↳ strong acids

* excellent solvents
* Protecting groups for alcohols

} ethers are:

* & they are good solvents; why?
1) Inert (لا يتفاعلون في التفاعل)
2) lowering E.A
3) polar & non polar parts (يذوبون النوعين)

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No.

$$CH_3CH_2-\overset{O}{}-CH_2CH_3 \xrightarrow{O_2} CH_3\underset{OOH}{CH}-O-CH_2CH_3$$

سلبية :

it forms peroxides

↓

cause explosions & its toxic

* peroxides are used in whitneing teeth.

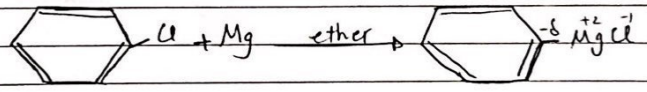
8.4 Grignard reagent

alkyl halide + Mg $\xrightarrow{ether}$ coupling reaction

(تفاعل تآلف واقتران ـــ Mg بتحطم الـ X)

big partial neg.

$$CH_3Br + Mg \xrightarrow{\ddot{O}:} \underbrace{\overset{-\delta}{C}H_3}_{Nu} \overset{+2}{Mg}Br^{-1}$$



* The Importance of it is prepairing a Nu carbon

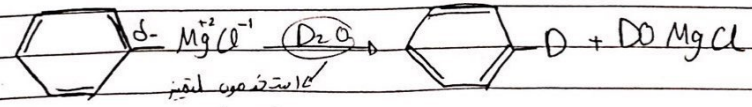
* فائدة الـ ether أنه يجعل غرينيارد مستقر

("الشحنة السالبة على C ليست كاملة بالتالي الـ Mg لم يتم معادلتها تماما")

$$CH_3Mg^{+2}Br^{-}$$

strong Nu = strong base ⟶ so if we had water : Gr will be corrupted

• $CH_3Mg^{+2}Br^{-} \xrightarrow{H-OH} \underbrace{CH_4 + HOMgBr}_{\text{I don't need these compounds}}$



كاستخدمون لتمييز

ما الذي يخرب G

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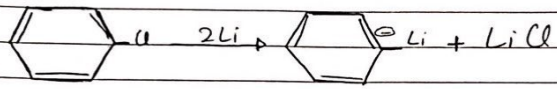
No.

* Any protic solvent destroy Gr.
* Thats why all conditions should be dry.

* بدل Mg ممكن نستخدم 2Li.



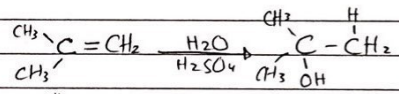
* Organometalic reagents → Ca

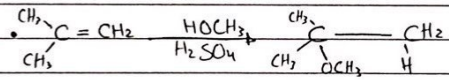
8.5 Preparation of ethers

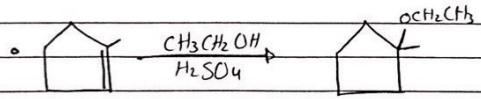
① $2\ CH_3CH_2OH \xrightarrow[150^\circ C]{H_2SO_4} CH_3CH_2OCH_2CH_3$

لذلك لم يحدث elimination

② From alkenes







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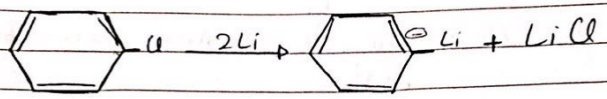
No.

* Any protic solvent destroy C_n.
* Thats why all conditions should be dry.

* بدل Mg ممكن نستخدم 2 Li.



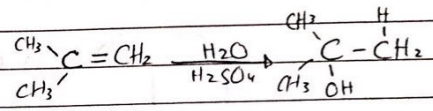
* Organometalic reagents → Ca

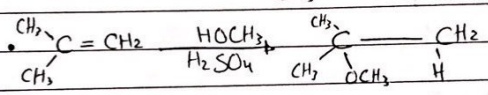
8.5 Preparation of ethers

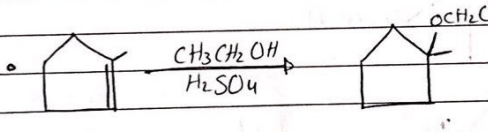
① $2\ CH_3CH_2OH \xrightarrow[150°C]{H_2SO_4} CH_3CH_2OCH_2CH_3$

elimination لذلك لم يحدث

② From alkenes







* Williamson Synthesis :

$RO^-Na^+ + {}'R-X \xrightarrow{SN^2} R-O-R'$

alkyl oxide — alkyl halide — ether

*strong Nu attacks the alkyl halide

Methyl — Methyl ← الشرط

1° أو — 1° أو

2° أو

~~3°~~

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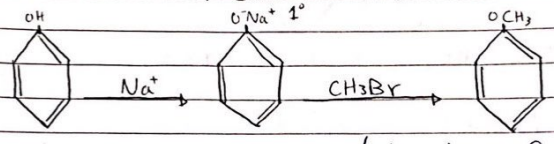
*primary alcohol doesn't react with HCl on its own

No.

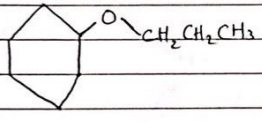
eg. $CH_3-\underset{H}{\overset{CH_3}{C}}-O^-Na^+ + CH_3CH_2\overset{Cl}{}$ (2° alcohol, 1° alkyl halide) $\longrightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-O-CH_2CH_3$

eg. $CH_3CH_2CH_2O^-Na^+ + CH_3CH_2\overset{Br}{}CH_2$ (1°) $\longrightarrow CH_3CH_2CH_2-O-CH_2CH_2CH_3$

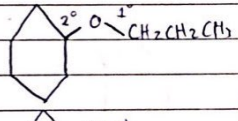
eg.



* We can prepare alkyl halide / alkyl halide from alcohols
- prepare this compound from the corresponding alcohols

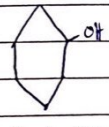


SOL:



$\overset{Cl}{}CH_2CH_2CH_3$

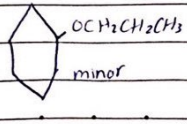
↑ Na, NaH ؛ ↑ PCl_5, $SOCl_2$ ؛ PB_3



$\overset{OH}{}CH_2CH_2CH_3$

* 2° alkyl halide doesn't work because what results is:

Major



minor

Major E2 → alken major

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No.

eg. $CH_3-C(CH_3)_2-O-CH_2CH_2CH_3$ → can't be prepared by williamson because its 3°

↓

3° alkyl halide + ionic Nu → %100 E_2

• $CH_3-C(CH_3)_2-Br + Na^+O^-CH_2CH_2CH_3$

↓

$CH_2=C(CH_3)_2$ %100 E_2

• $CH_3-C(CH_3)_2-O^-Na^+ + Cl-CH_2CH_2CH_3$

↓

$CH_3-C(CH_3)_2-O-CH_2CH_2CH_3$ + $CH_2=CHCH_3$

%15 %85

8.6 Cleavage of ethers : كسر الايثر

* Ethers are used in protecting other compounds like alcohols by turning this alcohol into ethers then we use "cleavage of ethers" We restore the alcohol.

* الايثر لا يتفاعل إلا مع acid وعلى low pH

* تنكسر الايثرات عند تفاعلها مع HI , HCl , HBr

$-\overset{|}{C}-O-\overset{|}{C}- \xrightarrow{HX} -\overset{|}{C}-OH \quad X-\overset{|}{C}-$

substitution reaction

• aromatic ether → واحد من الاطراف بنزين

• Aliphatic ether → الاطراف alkyl

Aromatic ether

Phenol البنزين يحمل (يأخذ OH) + alkyl halide (الالكيل يأخذ هالوجين)

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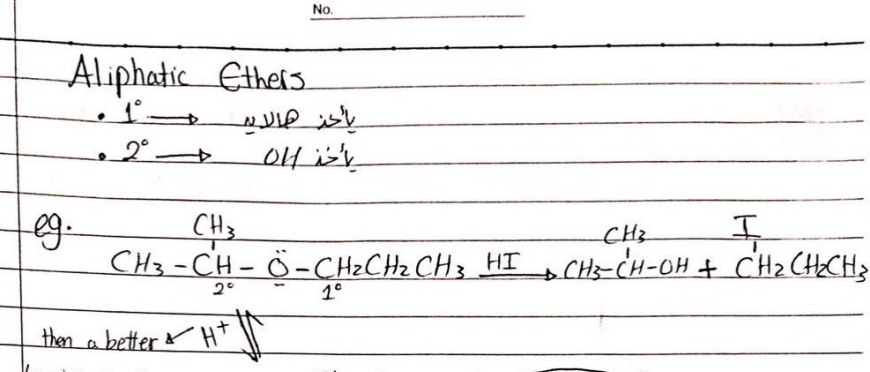
No.

Aliphatic Ethers

- $1^\circ \longrightarrow$ يأخذ هالايد
- $2^\circ \longrightarrow$ يأخذ OH

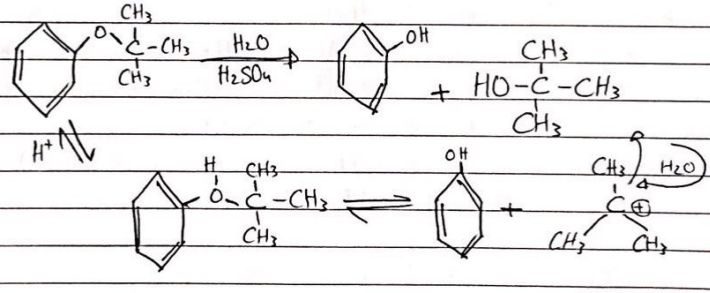
eg.



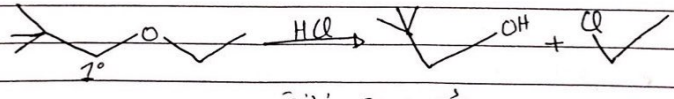
يهجم على الكربونة اللي عليها أقل اعاقة فراغية

- 2° $1^\circ \longrightarrow SN^2 \longrightarrow$ والهجوم على 1° لانه أسرع التفاعل عليها (OH تغادر على 2° ، I تهجم على 1°)
- $SN^2 \longleftarrow 1^\circ + 1^\circ$
- $SN^2 \longleftarrow {}^\circ 2 + {}^\circ 1$
- إذا أحد الكربونات $3^\circ \longrightarrow SN^1$

eg.



eg.



Cl^- يهجم على الأقل اعاقة فراغية

~~8.7~~ , ~~8.8~~ , ~~8.9~~ 8.10

End of second Exam

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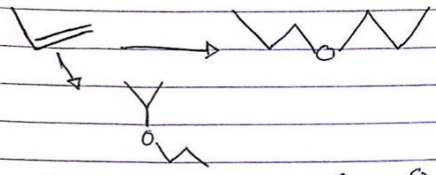
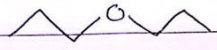
8+9

No.

H.W

- 
- $CH_3C\equiv C-H \longrightarrow$ 

CH 9 : Aldehydes & Ketones :

9.1 : Naming of Aldehydes & Ketones :

*They have priority over all functional groups aside from carboxyl groups

↳ in this case they beome subs.

eg. $CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-H$ 5-methyl hexanal

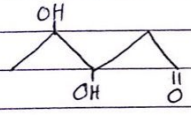
ما يشير إلى الألدهايد

* دائماً" كربونة الـ aldehyde رقمها واحد لأنها دائماً" على الطرف

eg. $CH_3CH=CH\overset{CH_2CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}-H$

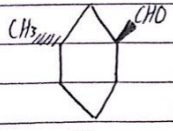
3-ethyl hex-4-enal ⟶ الجديد

3-ethyl-4-hexenal ⟶ الكتاب

eg. 

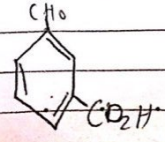
3,4-dihydroxypentanal

* cyclic Aldehyde ⟶ Cycle الـ alde دائماً" برا الـ

eg. 

trans-3-methylcyclohexancarbaldehyde

نسمي الـ cycle كما هي ثم نضيف carbaldehyde

eg. 

الـ aldehyde sub ك formal تسمى

m-formylbenzoic acid.

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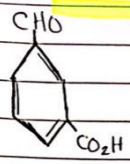
No.

"Haters are birds with clipped wings hopping around a cage telling the World that the sky isn't that great anyways"
-Atticus

eg. 

الـ aldehyde كـ subs تسمى formal

m- formylbezoic acid

* الأولوية للكيتون ولازم نحدد مكانه (لازم ما يكون فيه كربوكسيل)

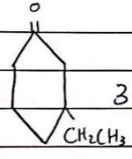
eg. $CH_3CH_2\overset{OH}{C}HCH_2\overset{O}{C}-CH_3$
4-hydroxy-2-hexanon

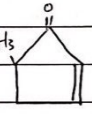
eg. $CH_3CH=CH-CH_2\overset{O}{C}-CH_2CH_3$
- 5-hepten-3-one — الكتاب
- hept 5-en-3-one — طريقة جديدة
الاثنين صح في الامتحان

eg. $CH_3\overset{O}{C}CH_2CH_2\overset{O}{C}-\overset{CH_3}{C}H-CH_2CH_3$
6-Methyl-2,5-octandiene

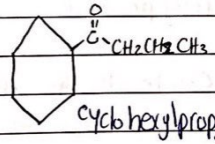
"The previous examples are Open Chain"

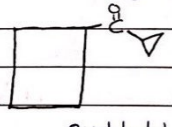
"Cyclic ↓"

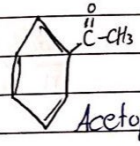
eg. 
3-ethylcycloheranone

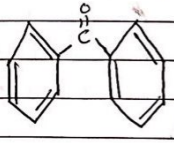
eg. 
5-methyl-2-cyclopentenone

* here Ketone is not part of the cycle but a sub (التسمية مثل طريقة تسمية الايثر)

eg. 
Cyclohexylpropyl Ketone

eg. 
Cyclobutyl cyclopropyl Ketone

eg. 
Acetophenone

eg. 
benzophenone

~~9/2~~

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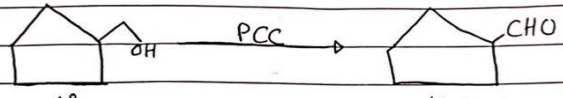
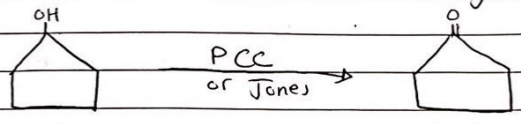
No.

9.3 preparation of Ketones & aldehydes

1 Oxidation of alcohols

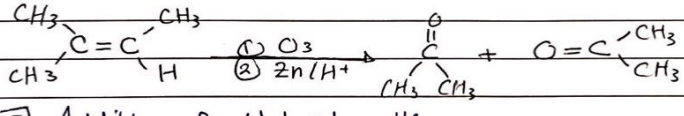


1° aldehyde

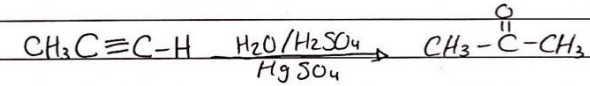


2° Ketone

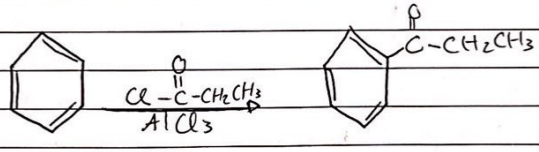
2 Ozonolysis of alkenes



3 Addition of Water to alkyne

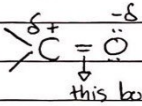


4 Acylation of benzene



9.5 Carbonyl group

*all the chemical / Physical properties of carbonyl Containing compounds come from the +δ on C & -δ on O.



this bond is highly polarized

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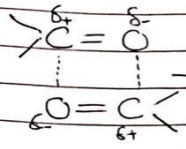
* الـ solub للـ aldehyde أعلى لأنه على الطرف فالتجاذب مع الماء أسهل.
* الـ BP للـ aldehyde أعلى لأن الـ Ketone يكون steric strain أكثر.

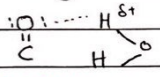
No.



→ dipole-dipole interaction
↓ very strong (partial charges higher than in ethers)
↓ hybridization : sp^2
↓ planar
↓ easier dipole-dipole interactions

*why does it have a strong dipole-dipole ?
-[1] high partial charges
-[2] planar

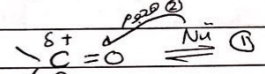
* They have solubility in water same as alcohols due to H-bonding with H_2O molecules.



*ما ينطبق على الكحول ينطبق عليه في موضوع الذائبية

Chemistry of Aldehydes / Ketones

9.6 Nucleophilic addition

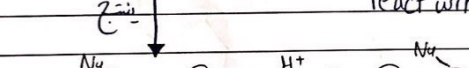


C is sp^2

electrophilic center — (partially + carbon wants to react with Nu)

③ يعلق الـ Pi
④ electrons of pi system goes to O

ينتج



C is sp^3 / tetrahedral Intermediate

* في الكيتونات والألدهايد تبقى O ثابتة وموجودة حتى تأثيرها H^+.
* يكون التفاعل أنشط كلما كانت +δ أكبر
* الخطوة التي يصير فيها فك الروابط في أول خطوة فكلما كانت +δ أكبر تكون أكثر جذب للـ Nu ويكون التفاعل أسرع.

* all compounds that have a carbonyl group react the same due to presence of +δ on C (Electrophilic center → Nu يجذب)

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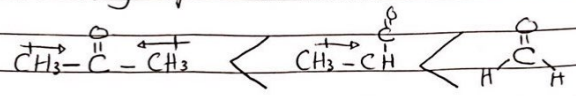
9

*less + δ → weak Electrophilic Center → less attractive to Nu
→ Slow rxn.

No.

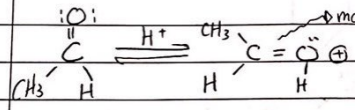
Reactivity upon Nu addition



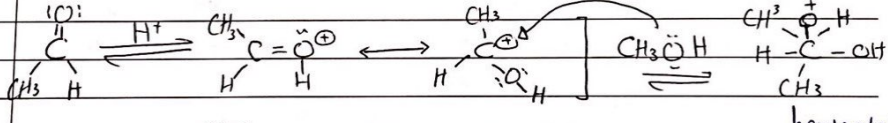
due to higher partial charge on electrophilic center

9.7 addition of alcohols (weak Nu) to Ketones & aldehydes

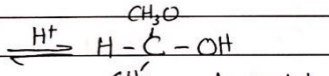
weak Nu + Aldehyde/Ketone → we need an acidic catalyst because the +δ on C is not attractive enough for a weak Nu



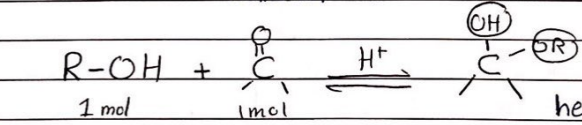
*protonated carbonyl is more reactive than carbonyl itself, why?
- because it has more + δ because
1. from oxygen 2. It has a resonance structure



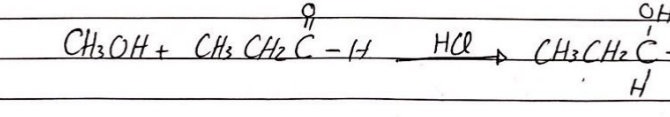
hemiacetal



hemiacetal



hemiacetal



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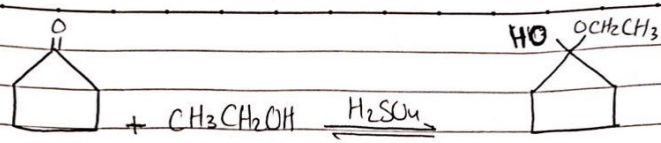
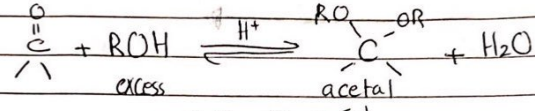
1 mol → hemiacetal

2 mol or excess → acetal

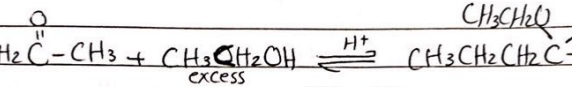
diaols + ether of aldehyde → cyclic acetal

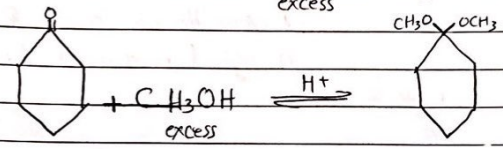
No.

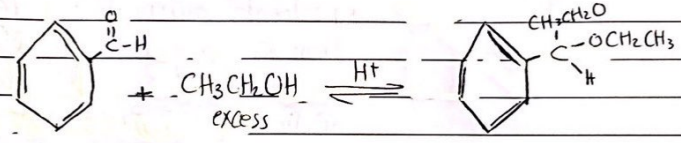


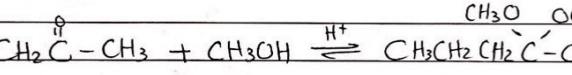


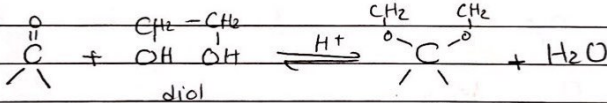
له کربون مرتبطه ب 2 ether

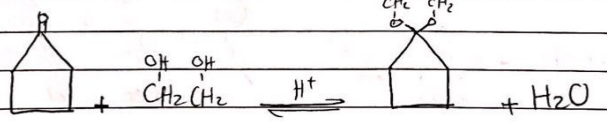


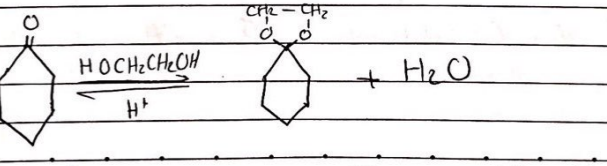












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No.

CH.10 Carboxylic acids

* Good News :) ⟶ naming carboxylic acid derivatives, ~~10.3~~, ~~10.5~~, ~~10.11~~, ~~10.22~~

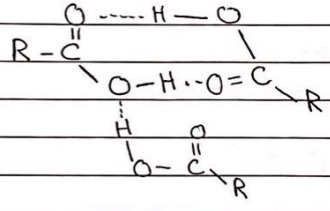
$-CO_2H$, $-COOH$, $-\overset{O}{\overset{\|}{C}}-OH$

10.2 Physical Properties

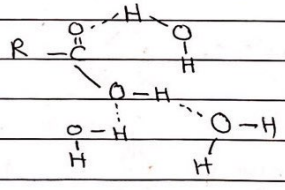
[1] They have the highest B.P in all organic groups.

[B.P] alkane = $R-\overset{O}{}-R$ < $-\overset{O}{\overset{\|}{C}}-$ < $R-OH$ < $R-CO_2H$

because ① They form strong hydrogen bonds
② can form hydrogen bonding from different sides.
③ Shape of carbonel group is planar which utilizes less steric strain which lets molecules fit more causing stronger hydrogen bonds.



[2] They have high solubility in water for the same reasons.



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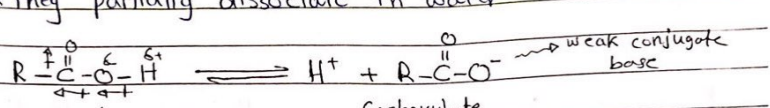
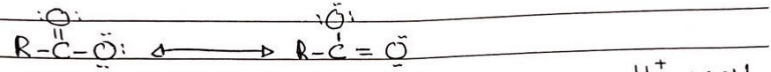
No.

* They partially dissociate in water



① high polarity ② has resonance structure thats why its stable



* stabe anion due to (R) effect → shift in eq → more H^+ → acid

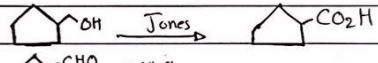
	CH_3OH		$CH_3C(=O)-OH$	HCl	$F_3CC(=O)-OH$
pKa	16	10	4.76	-7	0.23

generally weak acids / stronger than Phenols & alcohol

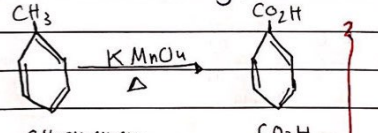
* يأثر على قوة المركب كحمض نفس العوامل المؤثرة على الأحول

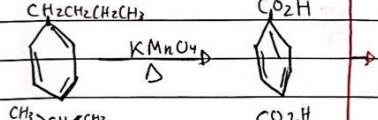
10.7 Preparation of carboxylic acids

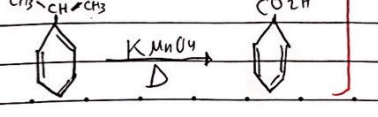
[1] Oxidation of 1° alcohol & aldehyde

- 1° alcohol  Jones
- aldehyde نفس الاوكسيدة

[2] Oxidation of alkyl substituted benzene

- 

- 

- 

→ The carbon attached to benzene is the one Oxidized (benzylic carbon)

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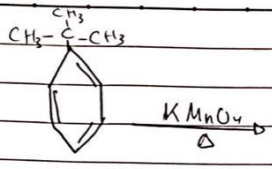
10

No.



3° carbon can't be oxidized so the benzene ring will be oxidized

*Carbon connected to benzen is oxidizied

*This carbon must have at least 1 carbon

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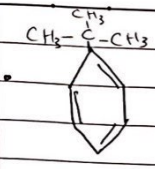
10

- Benzendicarboxylic acids are called phthalic acids
- O-phthalic → both Ortho
- iso phthalic → both meta
- Terephthalic → both Para

No.



$\xrightarrow[\Delta]{KMnO_4}$ $CH_3-\underset{CO_2H}{\overset{CH_3}{C}}-CH_3$ → 3° carbon can't be oxidized so the benzene ring will be oxidized

* Carbon connected to benzen is oxidizied
* This carbon must have at least 1 carbon
* ↓ جزء مدروس تم ارجاعه :"

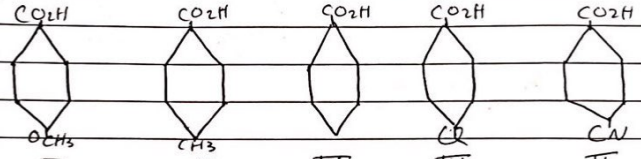
* Acidity of Carboxylic acid is same as for phenols & alcohols

eg. $ICH_2CO_2H < BrCH_2CO_2H < ClCH_2CO_2H < FCH_2CO_2H < F_3CCO_2H$

weaker AG / more EWG / stronger DG ← acidity ال ← *
stronger acid / more acidic / stronger acid

(least E.N → weakest acid)

eg.

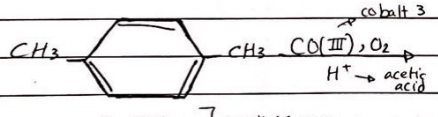


I II III IV V

Sol: I < II < III < IV < V

carboxylic acid عادي من acidity أكثر benzoic acid ال *
(conjugate base for it is weaker)

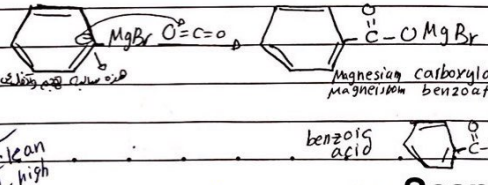
* Oxidation of Alkyl benzen :



$CH_3-C_6H_4-CH_3 \xrightarrow[H^+ \rightarrow \text{acetic acid}]{\text{cobalt 3}, O_2} HO_2C-C_6H_4-CO_2H$

p-xylene (Para) well-Known solvent → Terephthalic acid → industrial reaction → produced alot → starting material for Polymers like melamine

3 From Grignard reagent



$C_6H_5MgBr \xrightarrow{O=C=O} C_6H_5-C(=O)-OMgBr$

هزء سالب الحجم وتفاعل الرابطة

Magnesium carboxylate / magnesium benzoate

$\xrightarrow{H^+}$ benzoic acid

ميكانيكية

very clean reaction, high product

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*ملاحظة: عزيناريد مع كحول
H_2O
acetic acid
← يذوب عزيناريد ← للمهم protic

No.

(4) hydrolysis of cyano Compounds

- $R-CN \xrightarrow[H_2O/\Delta]{H^+} R-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$ (carboxylic acid, Amonium)

- $R-C\equiv N \xrightarrow[H_2O/\Delta]{OH^-} R-C-O^- + NH_3 \xrightarrow{HCl} R-\overset{O}{\overset{\|}{C}}-OH$ (carboxylate)

This reaction can happen in different condition → acidic → carboxylic acid (حامضي)
→ base → carboxylate → acidification → acid

- benzonitrile ($C\equiv N$) $\xrightarrow[\Delta]{NaOH/H_2O}$ Sodium benzoate ($C(=O)-O^-Na^+$) $\xrightarrow{HCl}$ benzoic acid ($C(=O)-OH$)
  (45-55 minute)
  after leaving it to cool we add HCl
  benzonitrile $\xrightarrow{OH^-/H_2O}$ benzamide ($C(=O)-NH$)
  benzamide $\xrightarrow{OH^-/H_2O}$ Sodium benzoate, $+ NH_3$ (base)

*هذا التفاعل يحدث على خطوتين فعليا"
الاول → benzamide

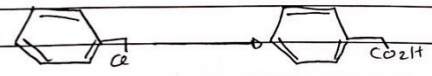
*إذا لم يكن التسخين كافي والمدة كافية يتحول
benzamide إلى carboxylate ولا يتحول كثير من

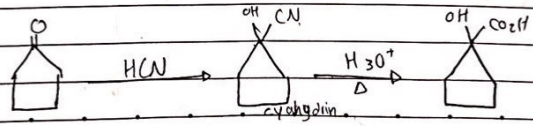
* 2 hydrolysis steps
* Not a straight forward reaction

- $CH_3CH_2CH_2Br \xrightarrow[DMSO]{K^+CN^-} CH_3CH_2CH_2CN \xrightarrow[\Delta]{HCl/H_2O} CH_3CH_2CH_2CO_2H$
  (a-polar, a-protic)

imp: eg. final: draw the structure of the main impurity in hydrolysis of benonitrite → benzamide

H.W.

- 

- 

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aldehyde & Ketone ⟶ nucleophilic addition

X : any of the previous groups

No.

10.4 acid derivatives : a group of compounds prepared from carboxylic acid.

- $R-\overset{O}{\overset{\|}{C}}-OH$ ⟶ we replace it with another group
- $R-\overset{O}{\overset{\|}{C}}-\boxed{\overset{\delta-}{O}CH_3}$ ⟶ alkyloxide — ester ——— التحضير (نحتاج الكحول)
- $R-\overset{O}{\overset{\|}{C}}-\boxed{\overset{\delta-}{O}-\overset{O}{\overset{\|}{C}}-R'}$ ⟶ carboxylate — acid anhydride ——— (نحتاج carboxylate)

  bond is polarized

  O, Cl, N in the rest ⟶ high E.N

- $R-\overset{O}{\overset{\|}{C}}-\boxed{\overset{-\delta}{Cl}}$ — -acyl chloride, -acid chloride
- $R-\overset{O}{\overset{\|}{C}}-\boxed{\overset{-\delta}{N}H_2}$ — amide ——— (نحتاج أمين أو أمونيا)

  أو أمين

- all these compounds are prepared from Carboxylic acids + they react as Nu Substitution

- $X-\overset{\delta-}{C}=O \xrightarrow{Nu} Nu-C-O^{\ominus}$ (X: $X^{\delta-}$)

  attacks & opens the pi system

  one pair form pi system & kicks X out

  $\rightleftharpoons Nu-C=O + X^-$ nucleophilic substitution

الخطوات : ① Nu attacks electrophilic Center

② Pi تفك ⟶ To form tetrahedral intermediate

③ O^- يكون ⟶ (in aldehyde / Keton the anion is stable but in acid derivatives its not stable because the bond is polarized)

④ O^- تطرد وترجع تكون Pi وتطرد X

* تسمية الايثر غير مطلوبة

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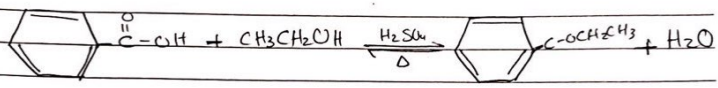
No.

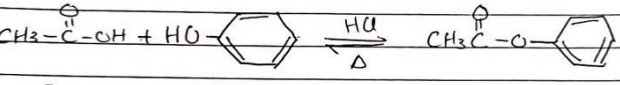
10.10 preparation of esters

- $R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$

fischer الطريقة

- $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OH \underset{H^+}{\overset{CH_3OH}{\rightleftharpoons}} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OCH_3 + H_2O$

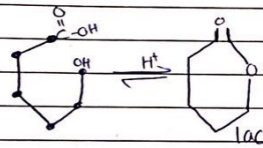
- 

- 

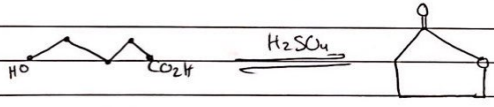
* Cyclic ester is called lactone

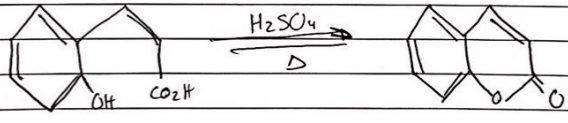
* نحسب النقاط ثم نرسم حلقة بعدها

* حلقة سداسية ثم نضع O

- 

lactone

- 

- 

10.13 Saponification

→ ester الـ hydrolysis ← fisher عكس

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[\Delta\ H_2O]{OH^-} R-\overset{O}{\overset{\|}{C}}-O^- + HOR'$$

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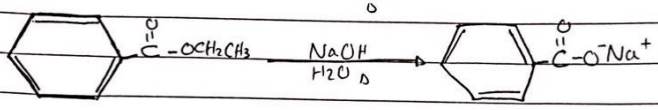
No.

- $CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow[H_2O,\ \Delta]{NaOH} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-O^-Na^+ + HOCH_3$

- 

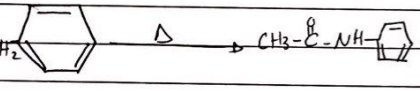
10.14 Ammonolysis

(تفاعل مع الأمين وتكوين أميد)

* لها دائماً نتيجة تفاعلات الاستركول

- $R-\overset{O}{\overset{\|}{C}}-O-R' \xrightarrow[\Delta]{NH_3} R-\overset{O}{\overset{\|}{C}}-NH_2 + HOR'$

- $CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[\Delta]{NH_2CH_3} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_3 + HOCH_3$

- $CH_3\overset{O}{\overset{\|}{C}}-OCH_2CH_3 +$ 

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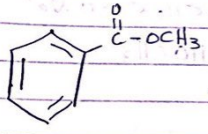
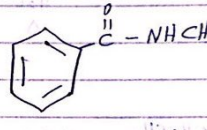
Ammonolysis

استر + أمين $\xrightarrow{\text{تسخين}}$ الأمين يهجم على الاستر و يستبدله و يكون أميد

$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \xrightarrow[\Delta]{NH(CH_3)_2} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-N(CH_3)_2 + HOCH_2CH_3$$

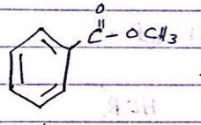
remove x and replace it by Nu





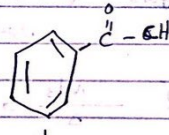
Reaction of Grignard with esters :

strong Nu



1 mol

CH_3MgBr (1 mol)



$+ \ \bar{O}CH_3$

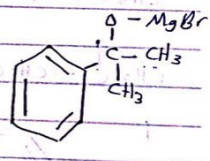
* ketone is more reactive than ester with grignard

* مجرد ما يتكون الكيتون يهجم عليه غرينيارد

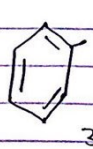
* ينتج في النهاية :

unreacted ester + traces of ketone + 3° alcohol

CH_3MgBr



H_3O^+



① CH_3MgBr excess

② H_3O^+

3° Alcohol

الاستر + excess grignard $\longrightarrow$ 3° alcohol

(لن يكون Chiral أبدًا لأنه يستقبل مرتين من Grignard)

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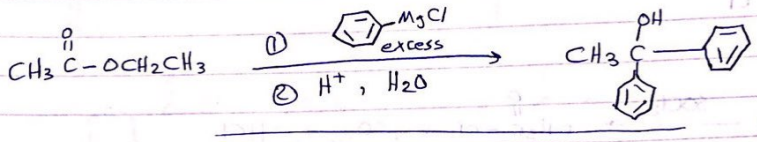
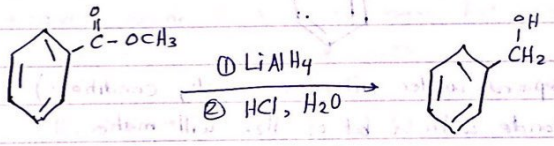
$$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{excess}]{① \; CH_3CH_2MgCl} \xrightarrow{② \; HCl,\ H_2O} CH_3CH_2CH_2CH_2\overset{O}{\overset{|}{C}}-CH_2CH_3 \quad (CH_2CH_3)$$



* كل كربونيل يتفاعل مع $LiAlH_4$ يتحول إلى كحول إلا الأمين يتحول إلى أميد

10.6 Reduction of esters

$$\underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} \xrightarrow[② \; H_3O^+]{① \; LiAlH_4} \underset{1^\circ \text{ alcohol}}{R-\overset{OH}{\overset{|}{C}}H_2} + HOR'$$



$$CH_2=CHCH_2\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \xrightarrow[② \; H^+,\ H_2O]{① \; LiAlH_4} CH_2=CH-CH_2\overset{OH}{\overset{|}{C}}H_3 + HOCH_2CH_3$$

Hydrolysis → acid catalysed
Hydrolysis → base catalysed

* alcoholysis of acid derivatives gives ester

acid derivative + H_2O ⟶ carboxylic acid

Alcoholysis التفاعل مع الكحول

alcohol + acid ⟶ ester

alcohol + carboxylic acid $\xrightarrow{H^+}$ ester $\xrightarrow[NaOH]{H_2O}$ carboxylate + alcohol

ester → amide ?

ester $\xrightarrow{\text{reduction}}$ 1° alcohol

ester → 3° alcohol ← grignard

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aldehyde / keton
Nu addition

alkene
electrophilic addition

acid derivatives
Nu sub

benzene
electrophilic sub

الكتاب

10.19 acyl chloride / acid chloride :

its the most reactive acid derivative

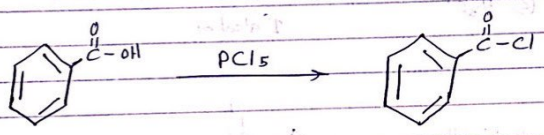
$R-\overset{O}{\overset{\|}{C}}-Cl$

eg. $CH_3\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} CH_3\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$

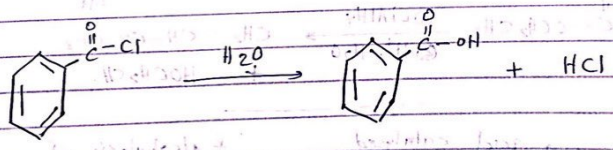
* pay attention here → you use $SOCl_2$ not HCl

* carboxylic acid + $SOCl_2$ → acyl chloride

eg.



* acyl chloride is prepared under nitrogen → (dry conditions) ,
→ because acyl chloride with a bit of H_2O will make it go back to being carboxylic acid



$CH_3\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{(Nu sub)}]{CH_3OH} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + HCl$

* acid derivatives can be prepared from each other
the less reactive is prepared from the more reactive
acyl chloride + alcohol → ester

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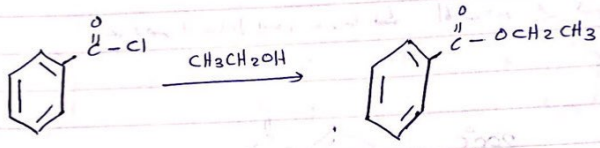
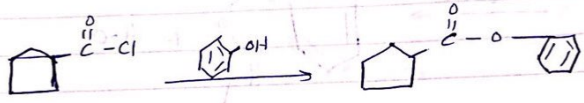
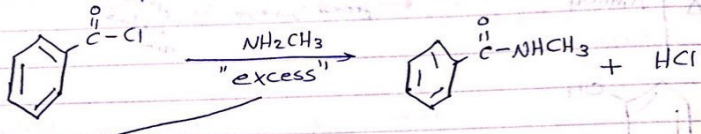
Acyl chloride is the most reactive ☆ مكرر

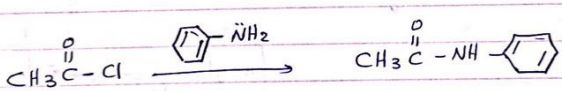




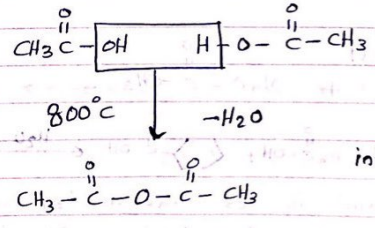


why ?

because amine is a strong base that reacts with HCl ويتثبط
so we have to add **2** moles



10.19 acid anhydride (the second most reactive after acid chloride)



التحضير من ال acid

inter molecular

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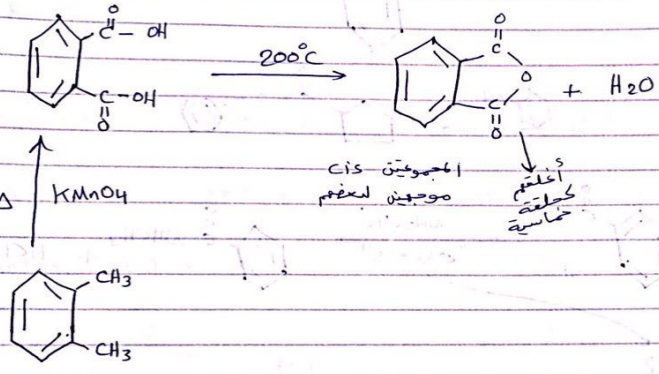
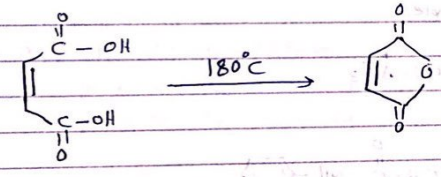
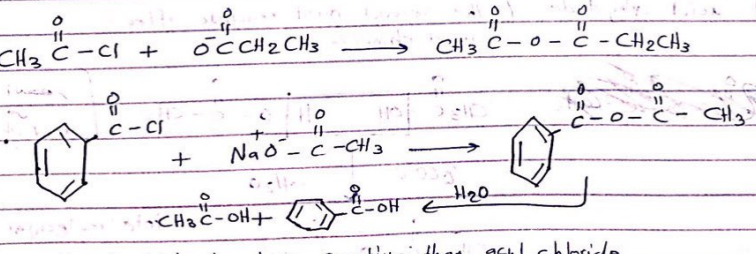
* يصير التفاعل أسهل عندما تكون المجموعتين في نفس الحلقة

intramolecular





تحضيره من acyl chloride



* acid anhydride is less reactive then acyl chloride
so we dont need to be extremly careful with it like acyl chloride

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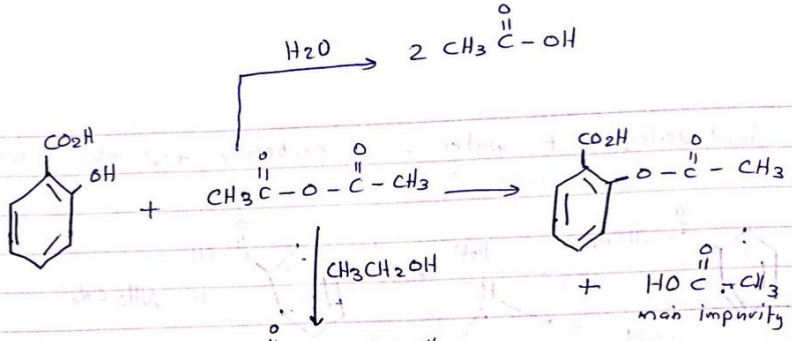
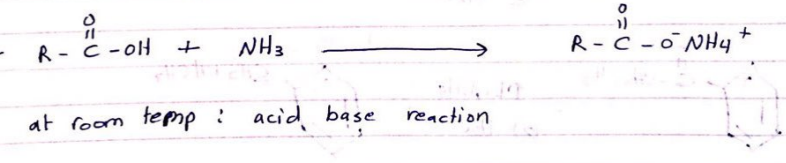
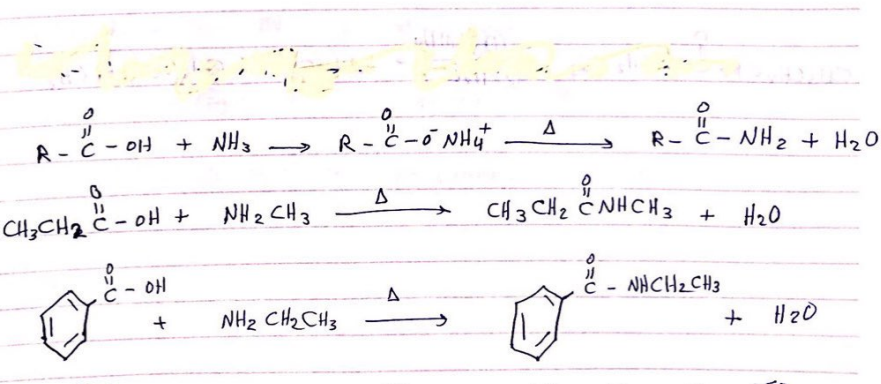


acid anhydride + كحول ⟶ ايستر

/// /// + phenol ⟶ ايستر

10.20 Amides (the least reactive acid derivatives)





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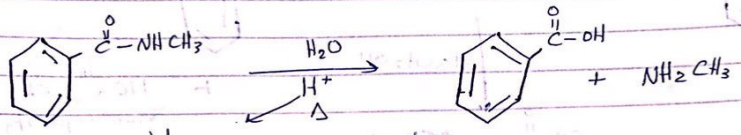
Acid derivative + water ⟶ carboxylic acid

eg.



acid

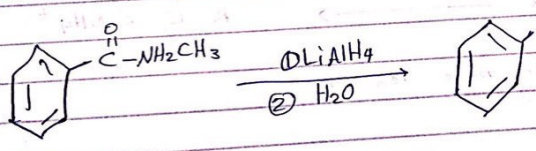
and also happens in basic conditions

* proteins are amides

eg. $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-NH_2CH_2CH_3 \underset{H_2O/\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OH + NH_2CH_2CH_3$

Reduction:

eg. $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{② } H_2O]{\text{① } LiAlH_4} CH_3CH_2CH_2\underline{CH_2}NH_2$



$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_3 \xrightarrow[\text{② } H_2O]{\text{① } LiAlH_4} CH_3CH_2CH_2\underline{CH_2}NHCH_2CH_3$

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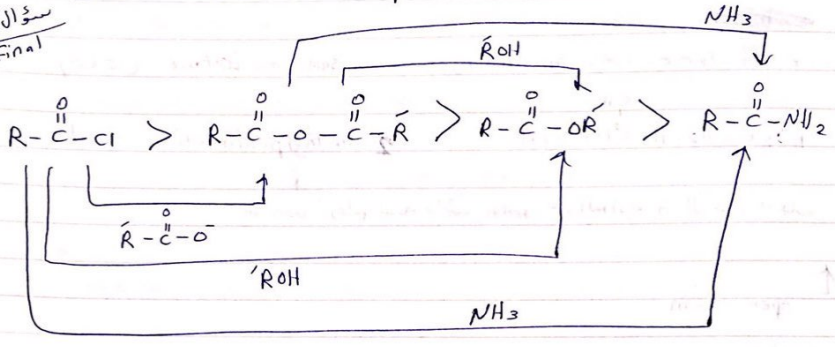
~~10.10 Anhydrides~~

* Reactivity of acid derivatives upon Na substitution reaction

سؤال مهم
Final



* Less reactive is prepared from the more reactive

* العملية العكسية دائماً تحتاج H^+

10.1 Naming of carboxylic acids (yes it was deleted then it came back :( )

* الازم نعد عدد ذرات الكربون و يكون الاسم منتهي ب acid oic

* دائماً ال oic هي #1

$CH_3CH_2CH_2CH_2C(=O)-OH$ pentanoic acid

$CH_2=CHCH_2CH_2C(=O)-OH$ 4- pentenoic acid

$CH_3C(=O)-CH_2CH_2CH_2C(=O)-OH$ 5- oxohexanoic acid

الكيتون
derivative
(oxo)

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$CH_3\overset{OH}{\overset{|}{C}}H\,CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$ 4-hydroxypentanoic acid

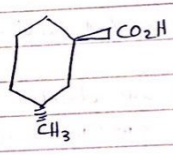
* If there was an aldehyde ⟶ same as ketone (oxo)

$HO_2CCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCO_2H$ 2-methylpentandioic acid

من دون أرقام لأنه دائماً واحد في البداية و الآخر في النهاية

open chain

cyclic ⟶



trans-3-methylcyclohexancarboxylic acid

end of Chapter

~~117~~ ~~119~~ ~~113~~

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Chapter 11 : Amines

* I'll deal with the amine as if its a substituent

11.1 Naming of Amines

$R-\ddot{N}H_2$

sp^3, has $2e^-$ which makes it a base

$CH_3\underset{}{CH}(NH_2)CH_2CH_3$ 2- aminobutane (1° amine)

$CH_3CH_2CH(N(CH_3)_2)CH_2CH_2CH_2CH_3$ 3- N, N- dimethyl amino heptane (3° amine)

لأن كلا CH_3 على N

(لدينا مجموعتين هغار و مجموعة كبيرة من الكاربون)

$(CH_3CH_2)_3N$ tri ethyl amine (3°)

(لدينا ٣ مجموعات متطابقة)

$(CH_3CH_2CH_2CH_2)_2NH$ di butylamine (2°)

1° / 2° / 3° ⟶ تعتمد على عدد ذرات الكربون المرتبطة بال N نفسها

* الأمين ليس لها أي أولوية
* نتعامل معها كـ sub إلا إذا كانت مثل حالة di, tri

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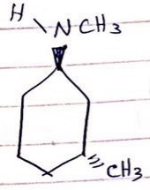
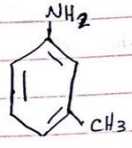


trans- methyl -3- N- methylaminocyclohexane

* its cyclic, by default the earlier alphabatical order has # 1



m- methyl aniline

N- methyl aniline

11.3 Physical properties of amines :

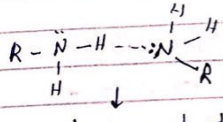
* Boiling points of amines are less than boiling points of alcohols

$CH_3CH_2CH_2NH_2$ > $CH_3CH_2\overset{H}{N}CH_3$ > $CH_3-\underset{CH_3}{N}-CH_3$

1° — strongest H - bonding
- 2 (N-H)

2° — weaker H- bonding

3° — No H- bonding
- (No N-H bonds)
- more branched (highly branched)



branching increase →

↓ hydrogen bonding together

① H - bonding
② branching

] factors that affect B.P

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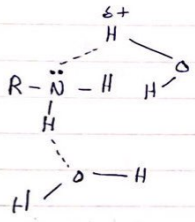
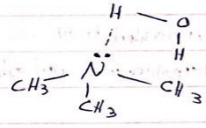
* amines have solubilities in water



In 3° amine :
* lone pair of e^- on N form hydrogen bonding with water but no H-bonding with eachother

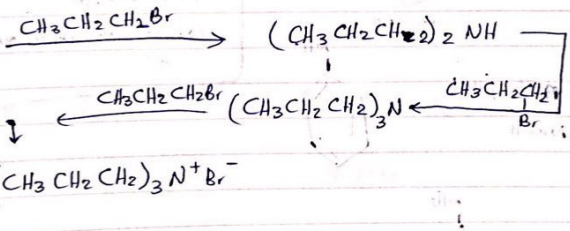


H.4 nucleophilic substitution in amines

$$CH_3CH_2\underset{\underset{Br}{|}}{CH_2} \xrightarrow{\ddot{N}H_3} CH_3CH_2CH_2\underset{\underset{NH_2}{|}}{} \qquad (SN_2)$$

1° alkyl halide

amine ↓ (its stronger than NH_3 as a Nu)



* the reaction is not selective, we get a mixture

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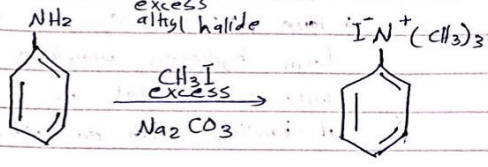
* آخر تفاعل في الكتاب ☆ final

تحضير 4 خطوات

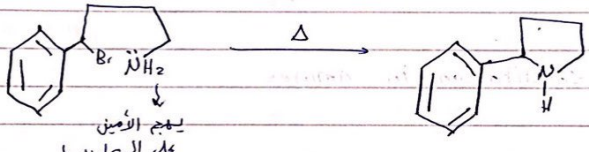
* طريقة مفيدة لتحضير Quarternary amonium salt ، وليس secondary ، ——



* عند إعطاء حرارة أقل يحدث التفاعل intramolecular (داخل المركب)

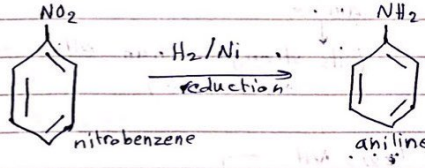
(حرارة أعلى ← intermolecular أي بين المركبات)

فينتج Cyclic amine



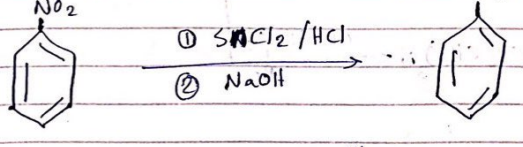
يهجم الأمين على الـ halide

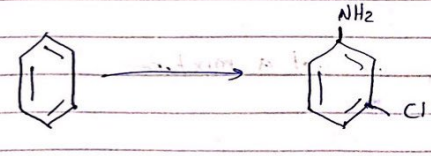
11.5 preparation of amines



nitrobenzene — aniline

* Nu sub of amines
  - → works only for intramolecular
  - → intermolecular → تعطي لي أو أعطيه excess حتى يعطيني الـ Quaternary amonium salt



eg. 

prepare.

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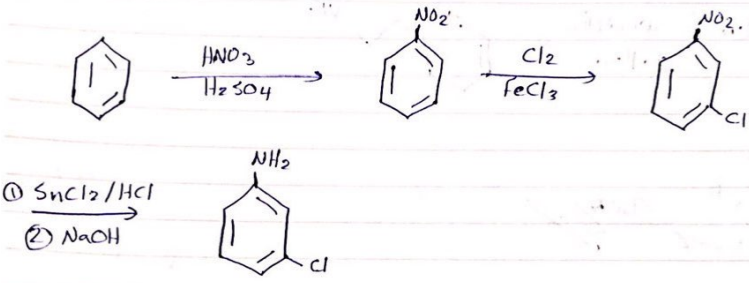
① NH_2 → ortho / para

② Cl → ortho / para

③ العلاقة بينهم meta

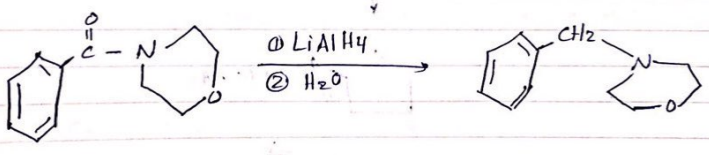
* NO_2 تحفز من compared to NH_2

Sol :



② Reduction of amides

$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-NH-CH_3 \xrightarrow[\text{② } H_2O]{\text{① } LiAlH_4} CH_3CH_2CH_2CH_2NHCH_3$$



③ Reduction of cyano compounds

$$R-CN \xrightarrow{H_2/Ni} R-CH_2NH_2$$

$$R-CN \xrightarrow[\text{② } H_2O]{\text{① } LiAlH_4} R-CH_2NH_2$$

$$CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}H_2 \xrightarrow[DMSO]{KCN} CH_3CH_2CH_2\overset{CN}{\overset{|}{C}}H_2 \xrightarrow{H_2/Ni} CH_3CH_2CH_2CH_2CH_2NH_2$$

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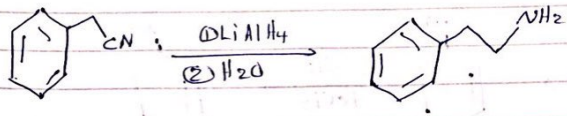

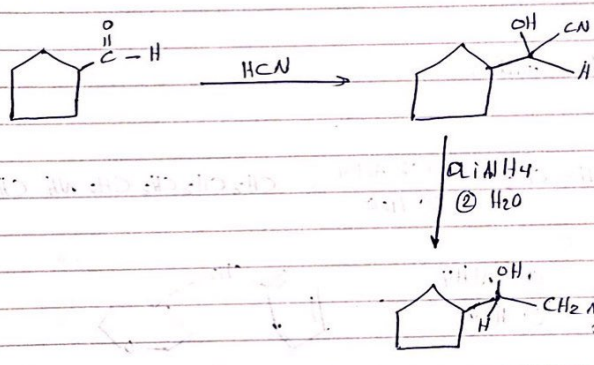

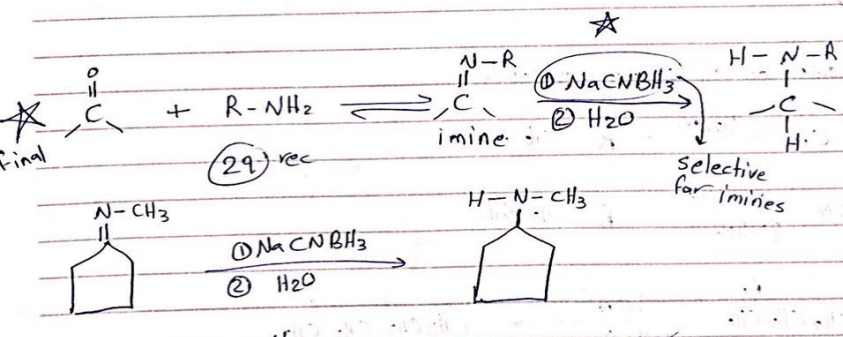

imine : $\overset{N}{\overset{\|}{C}}$ → has a special reducing agent

① Na CNBH3 (sodium syanoburane

② H2O

its selective to imine → reduces it to amine

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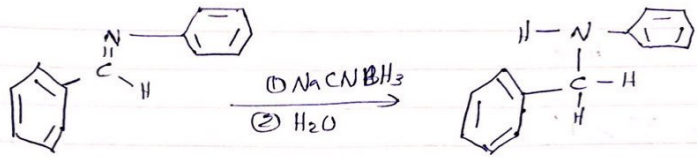
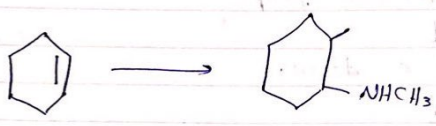


H.W



11.6 Basicity of amines

$-\ddot{N}\backslash$ Electron lone pair donors

* الدلالة على القاعدية نستخدم pka للـ conjugate acid.

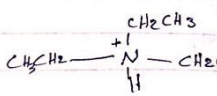
$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + OH^-$$

conjugate acid

strong base ← high pka (weak acid)

weak base ← low pka (strong acid)

		pka
$CH_3CH_2\ddot{N}H_2 \xrightleftharpoons{H_2O} CH_3CH_2\overset{+}{N}H_3 + OH^-$		10.75
$(CH_3CH_2)_2\ddot{N}H \xrightleftharpoons{H_2O} (CH_3CH_2)_2\overset{+}{N}H_2 + OH^-$		10.98
$(CH_3CH_2)_3\ddot{N} \xrightleftharpoons{H_2O} (CH_3CH_2)_3\overset{+}{N}H + OH^-$		10.76



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stronger as base

$2^\circ > 3^\circ > 1^\circ$

In 3°: 3 electron releasing groups

↓

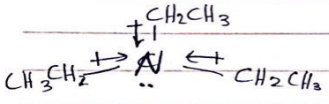
high e^- density

↓

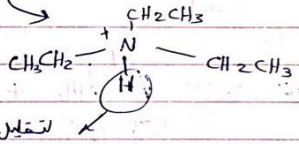
more repulsive power

↓

stronger base



less stable due to steric strain



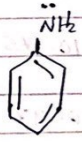
لتقليل ال strain تعطي ال H

↓

stronger acid

↓

weaker base



4.76

delocalized $2e^-$
less e^- density

10.7

↓

localized $2e^-$
high e^- density
stronger base

* aromatic amines are weaker as a base than aliphatic amines (amines are stronger as bases than anilines)

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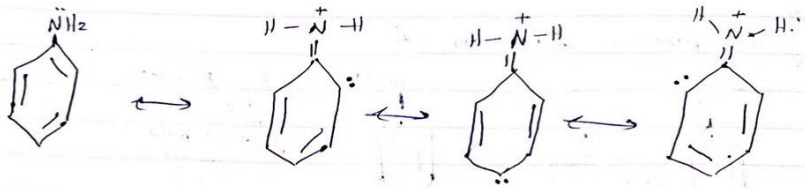
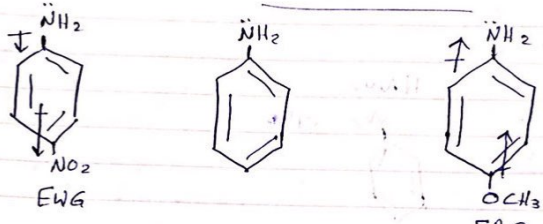
amines > aniline as a base





low e^- density
weaker base

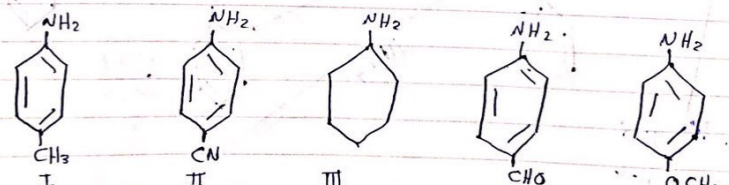
high e^- density (at N)
stronger base

Aniline as a base:

EWG < < ERG

* stronger ERG → stronger base
* stronger EWG → weaker base

eg.



Sol: ~~III is the strongest~~

III > V > I > IV > II

11.7 11.8 ~~11.9~~ 11.10 11.11

I ac
II de
III
IV de
V Ac

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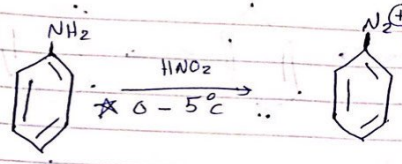
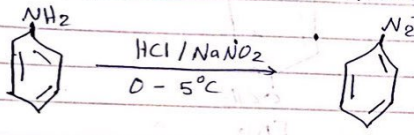
11.12 Aromatic diazonium salt

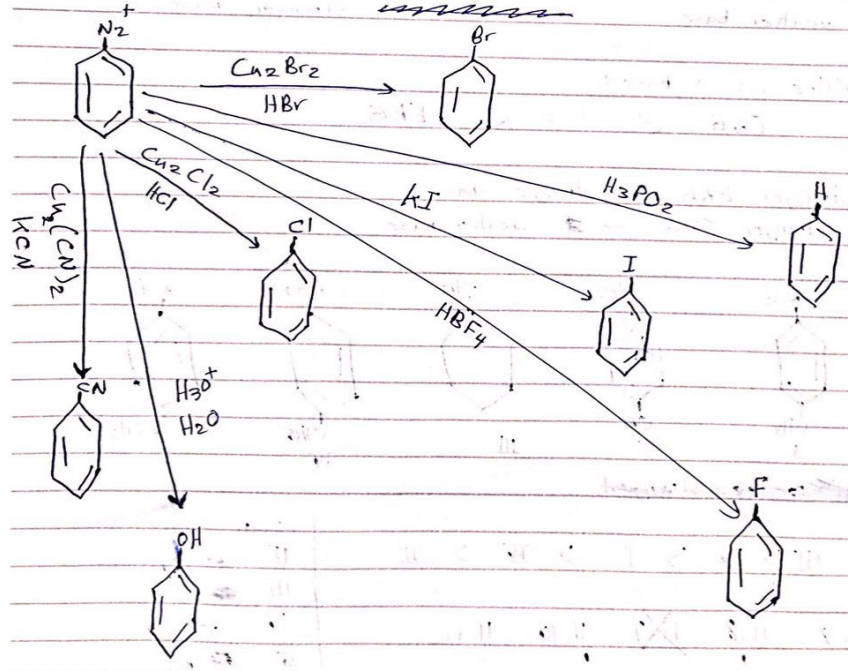


مسلمن N2
على غير البنزين
لحتما على البنزين
مستقرة
أكثر

$$HCl + NaNO_2 \longrightarrow HNO_2$$



benzendiazonium chloride



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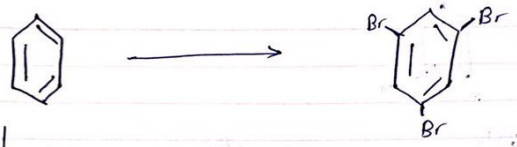
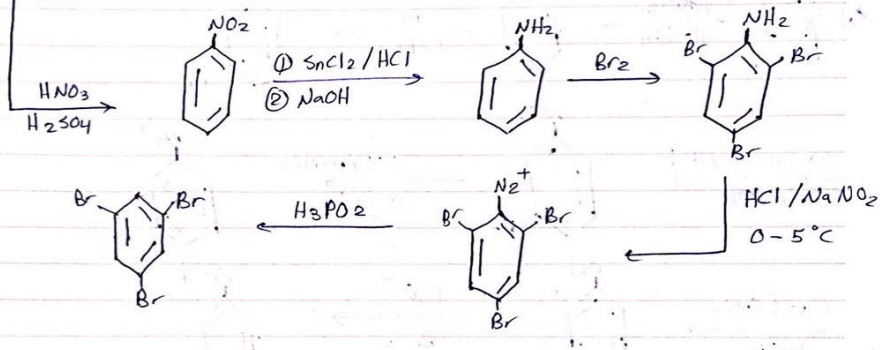
reduction of nitro benzene ⟶ aniline

eg.

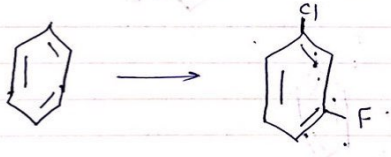


prepare

sol :

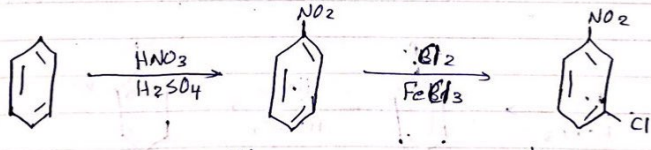


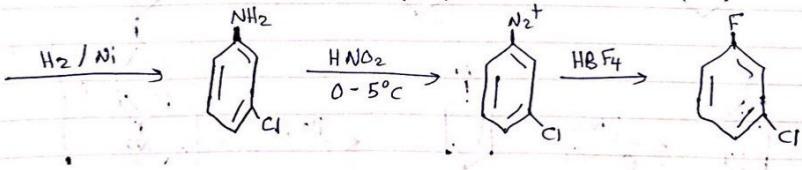
eg.



meta di-halo

sol





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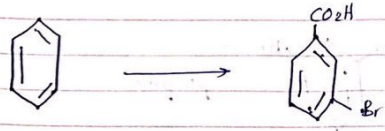
* أي Sub على البنزين يتفاعل على شكل elec aromatic sub

eg.



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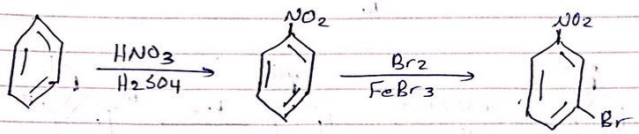

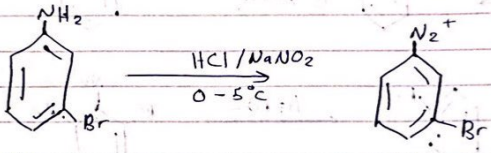

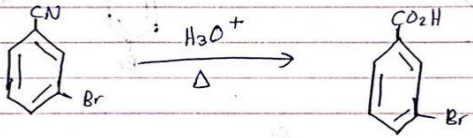

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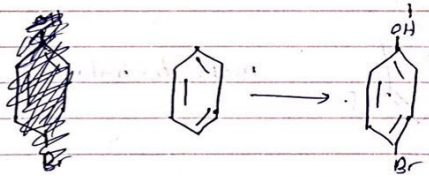

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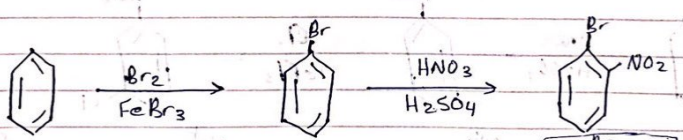

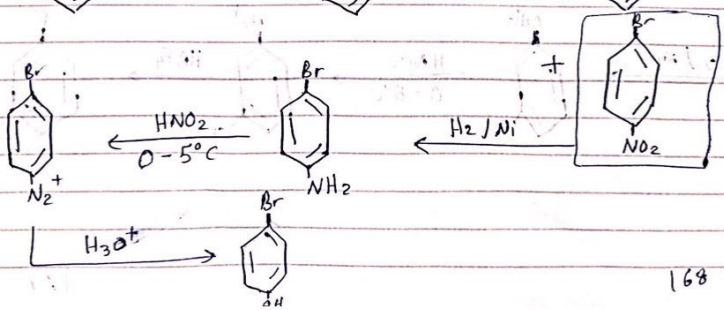

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