الجمهورية الجزائرية الديمقراطية الشعبية

وزارة التعليم العالي و البحث العلمي

جـــامـــعـــة الشهيد حمه لخضر – الـــوادي

قسم الكيمياء

السنة أولى ماستر كيمياء الدورة العادية

امتحانات السداسي الاول

المقاييس:

- Chimie organique1
- Informatique pour la chimie
- Anglais
- Chimie analytique des réactions couplées
- Stratégies et outils en Synthèse organique
- Chimie organique quantique
- Les réactions fondamentales de la chimie organique

الموسم الجامعي : **2017/2016**

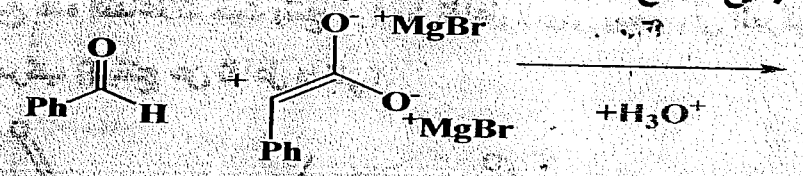
جامعة الشهيد حمه لخضر الوادي
كلية العلوم الدقيقة
قسم الكيمياء
سنة أولى ماستر كيمياء عضوية

السنة الجامعية 2017/2016
المادة:التفاعلات الأساسيةفي ك.ع
المدة :1ساعة و30 د

امتحان في مادة
التفاعلات الأساسية في الكيمياء العضوية

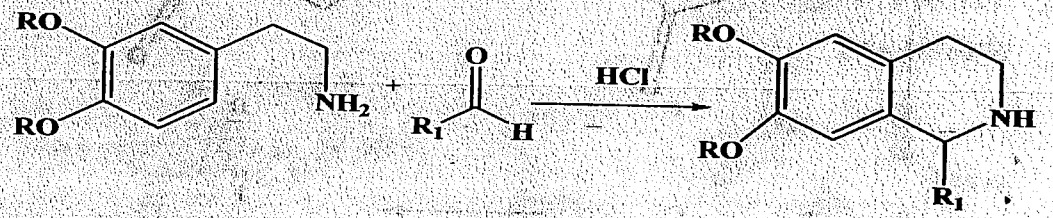
التمرين الأول (11) :

أ- أعط جميع النتائج المحتملة لهذا التفاعل مع توضيح الآلية ؟

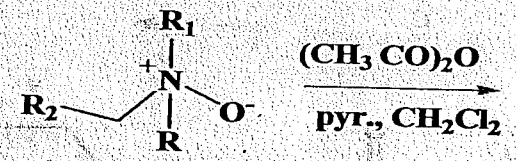


ب- أعط مراحل وآلية تفاعل الحصول S-2-ethylhexanal انطلاقا من butanal ؟

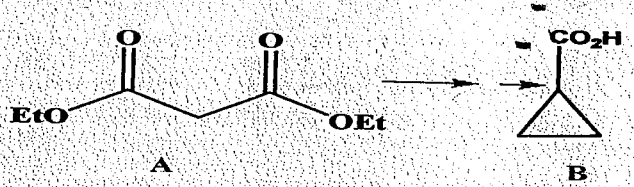
ت- أعط أليه التفاعل التالي ؟



ث- اتمم التفاعل التالي مع أعطاء الآلية ؟

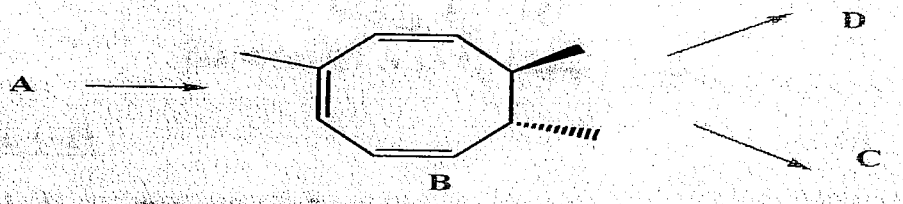


هـ- أعط مراحل وآليات تفاعل الحصول علىB انطلاقا من A؟

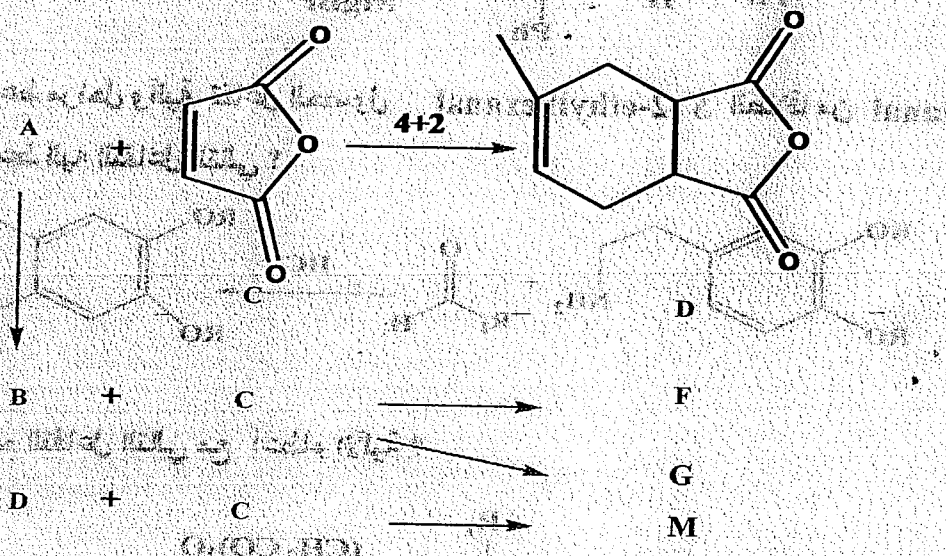


التمرين الثاني (9):

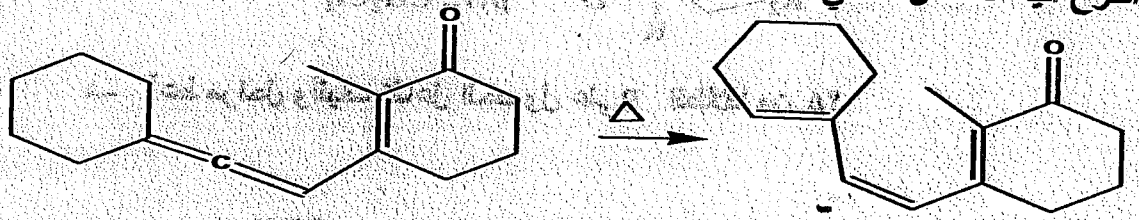
أ- أعط آلية وتتائج هذه التفاعلات حيث ينتج C و B من تفاعل ضوئي بينما ينتج D من تفاعل حراري؟



ب- أعط آلية وتتائج هذه التفاعلات حيث ينتج G من تفاعل ضوئي بينما باقي المركبات تنتج من تفاعلات حرارية المركب B ينتج عن تفاعل داخلي؟



د - اقترح آلية للتفاعل التالي ؟



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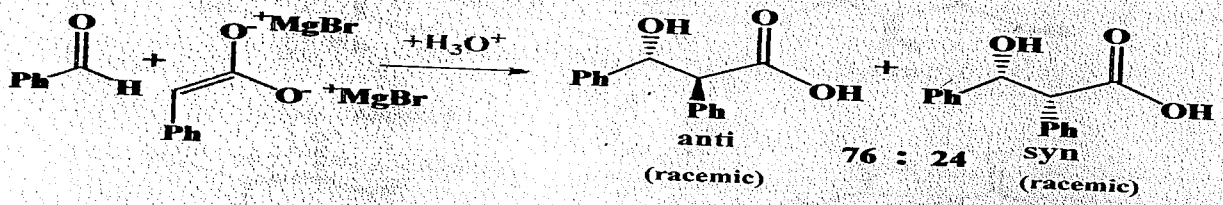
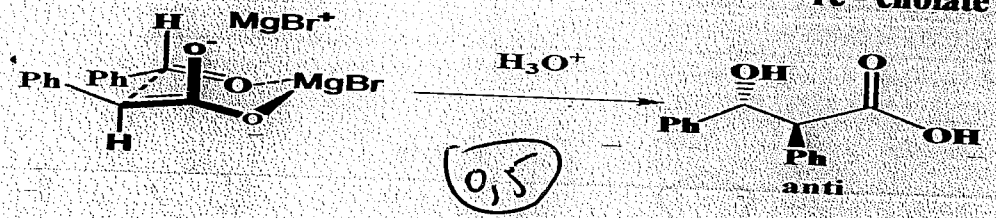
حل امتحان التفاعلات الأساسية في الكيمياء العضوية

حـل التمرين (11) :

أ-

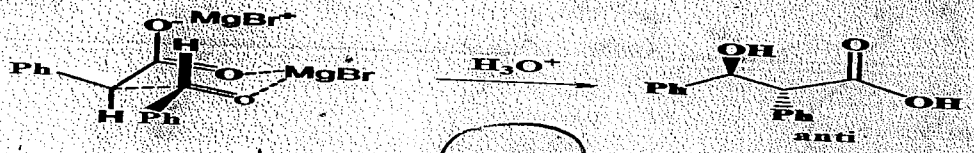


1)-جهة re -PhCHO مع
جهة re - enolate



0,5

2)- جهة si - PhCHO مع
جهة si - enolate

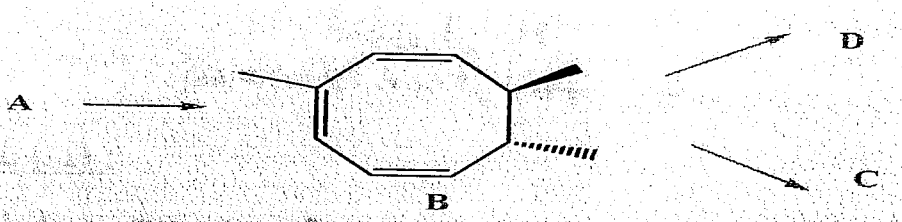


0,5

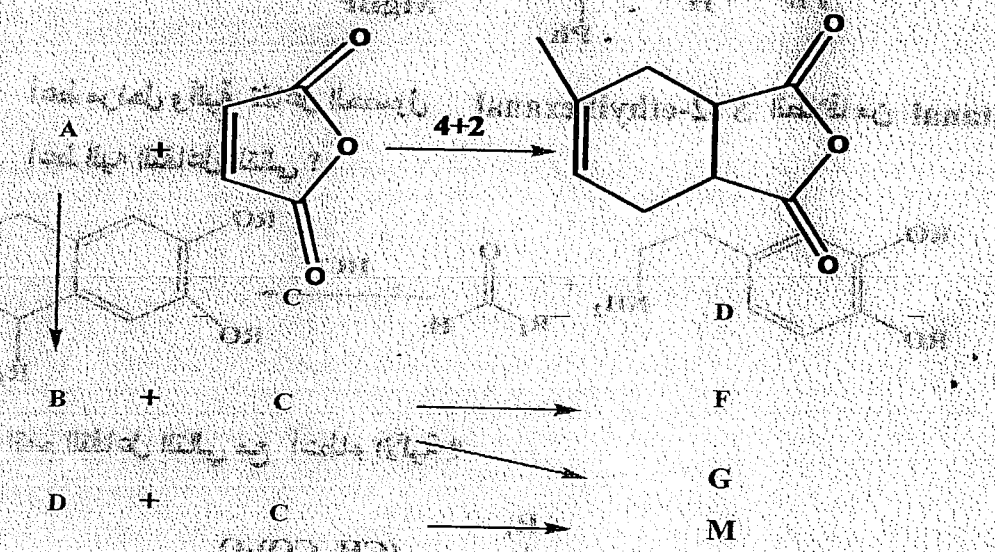
3)- جهة re -PhCHO مع
جهة si - enolate

التمرين الثاني (9):

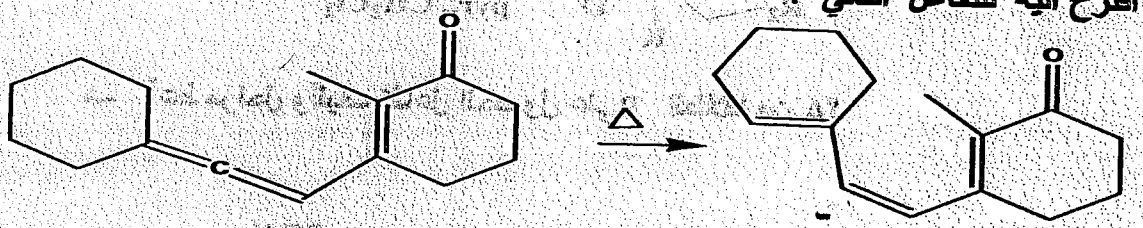
أ- أعط آلية وتتالي هذه التفاعلات حيث ينتج C و B من تفاعل ضوئي بينما ينتج D من تفاعل حراري؟

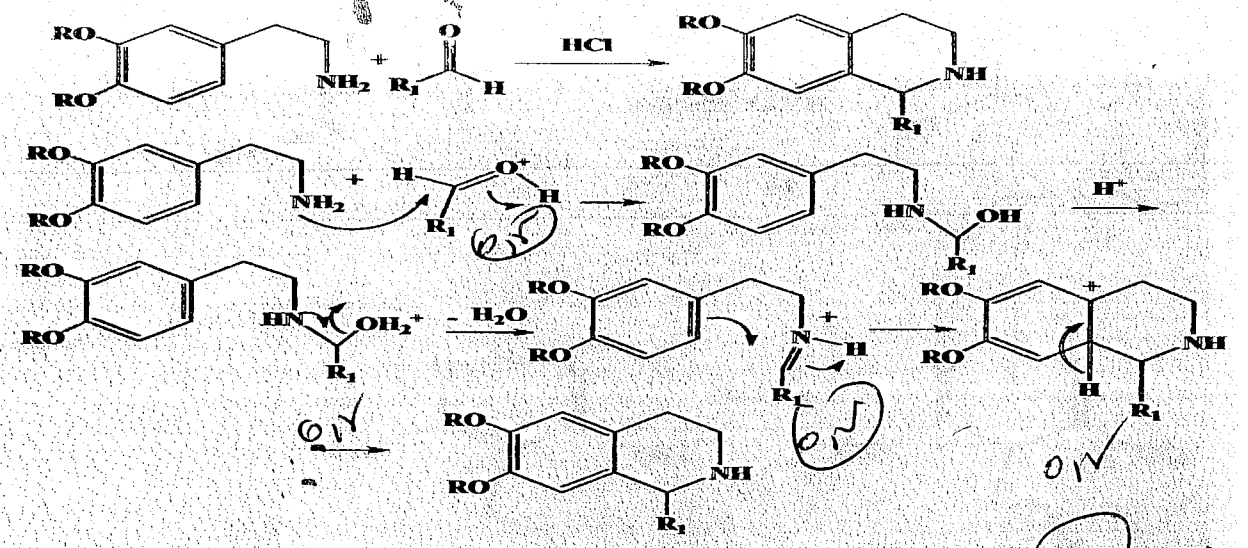


ب- أعط آلية وتتالي هذه التفاعلات حيث ينتج G من تفاعل ضوئي بينما باقي المركبات تنتج من تفاعلات حرارية المركب B ينتج عن تفاعل داخلي؟

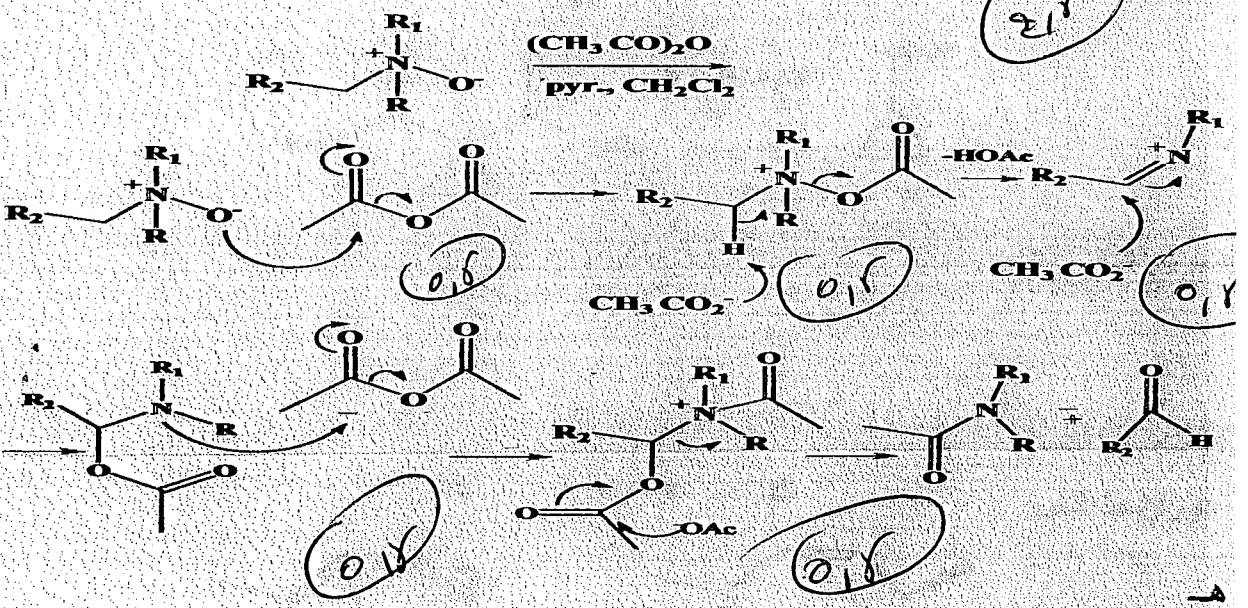


د - اقترح آلية للتفاعل التالي ؟

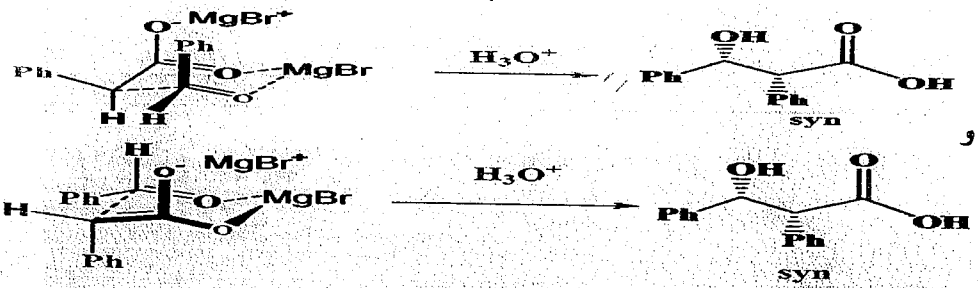




ث-



هـ

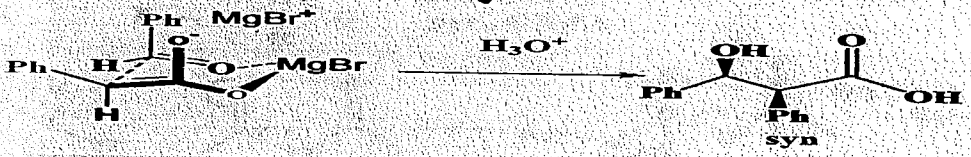


و

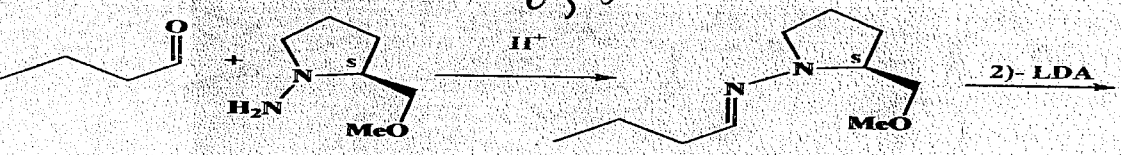
4)- جهة re - enolate مع

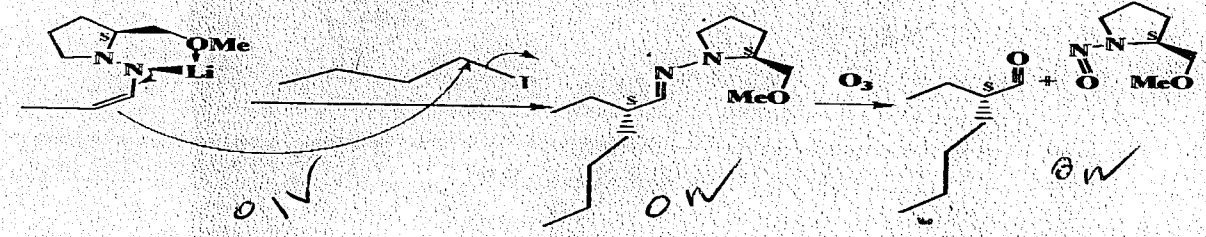
جهة si =PhCHO

و

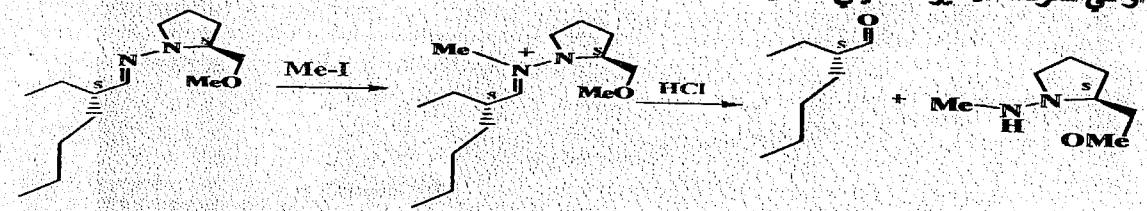


ب-

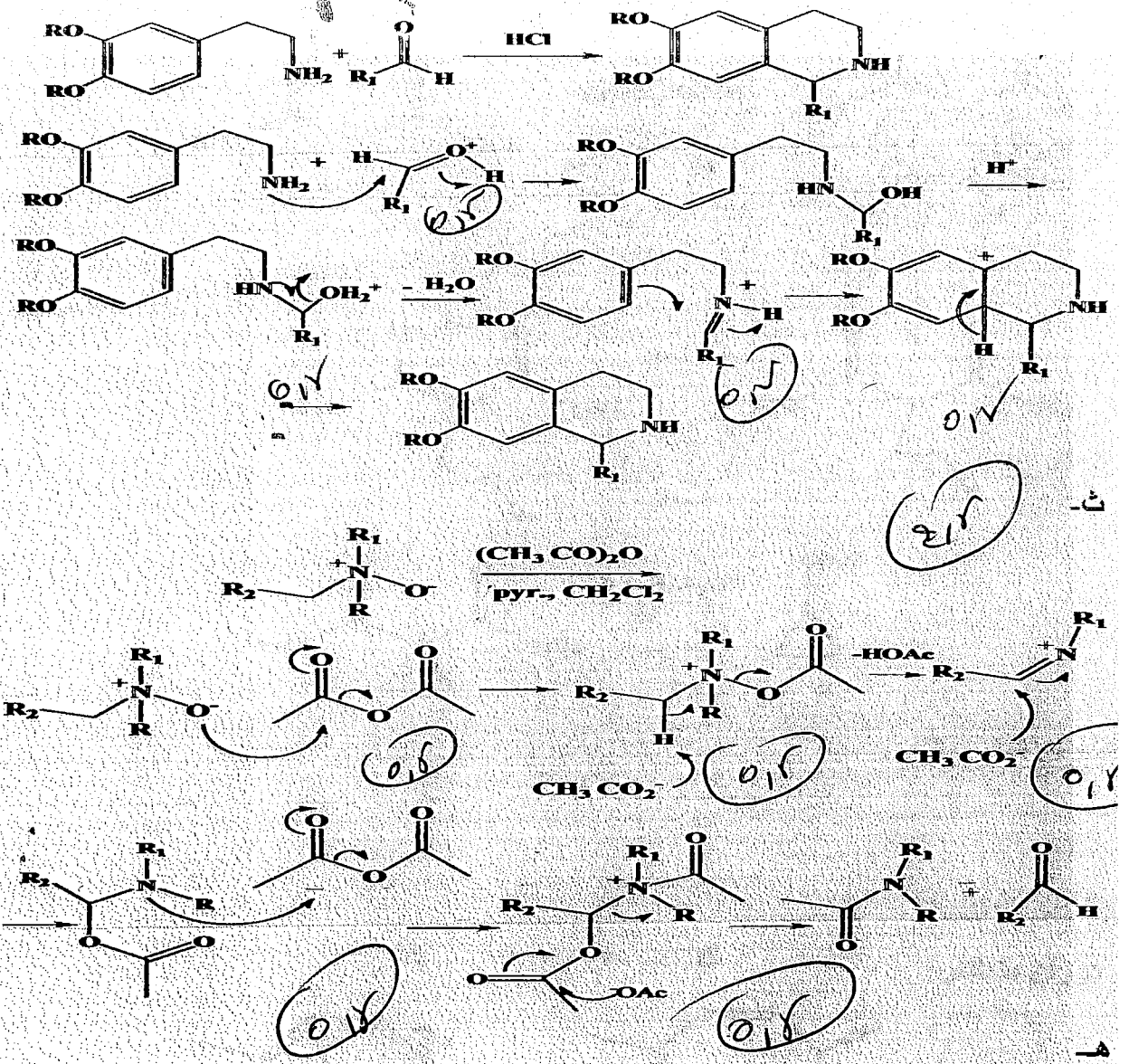


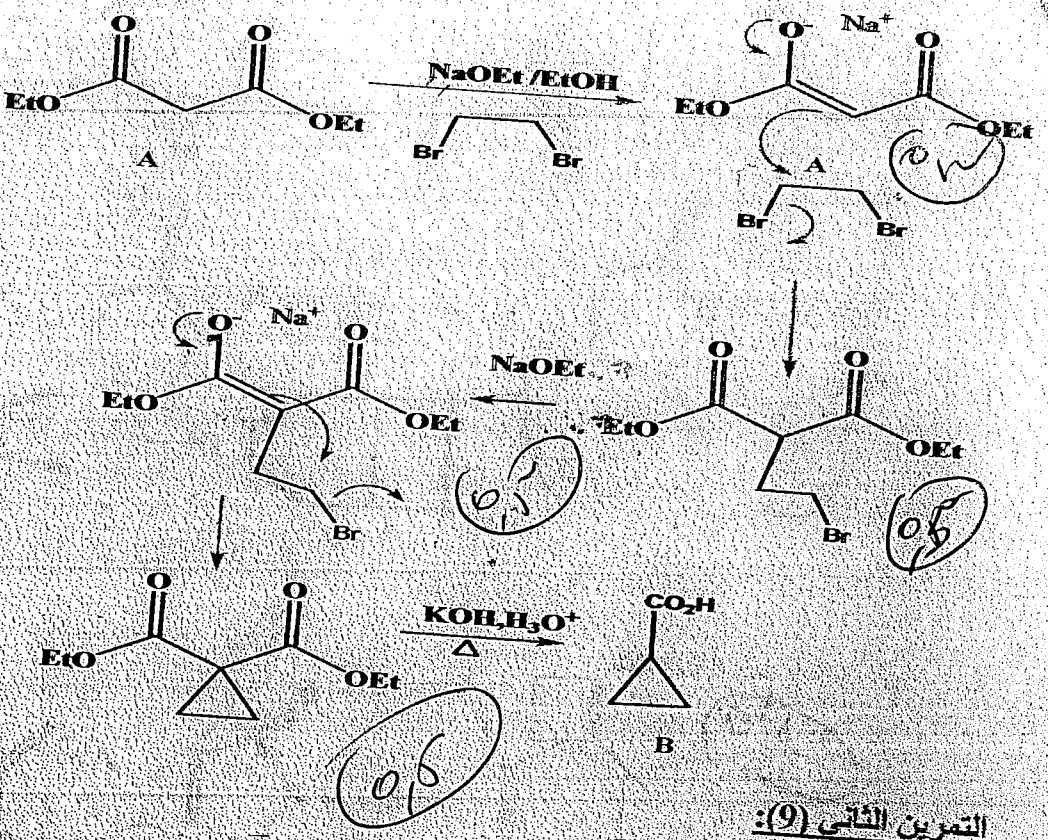


أو في المرحلة الاخيرة كمايلي -



ت -


HCl
$(CH_3CO)_2O$
pyr., CH_2Cl_2
-HOAc
$CH_3CO_2^-$
$-H_2O$
H^+



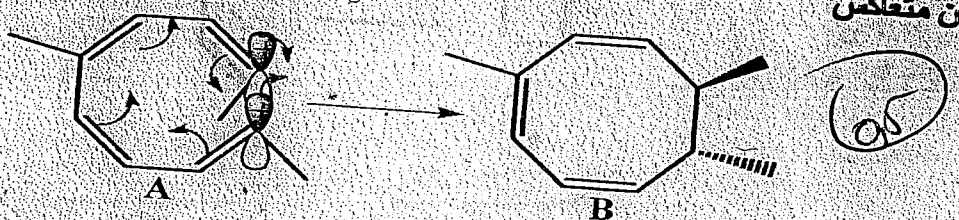
التمرين الثاني (9):

أ-

التفاعل الضوئي :

A ⟶ B

دوران متعاكس

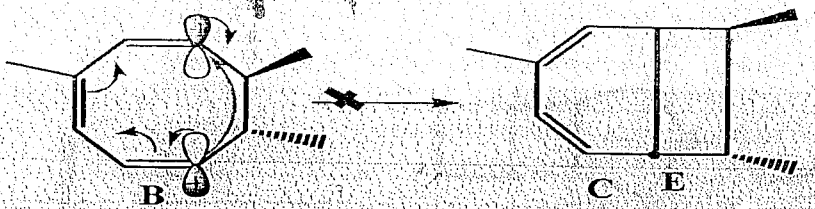


التفاعل الضوئي:

B ⟶ C

دوران متحد

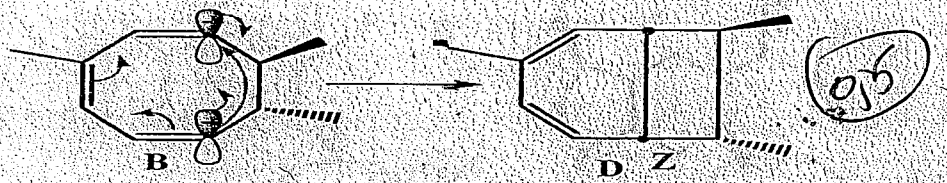
وهو تفاعل غير مسموح لتكوين الحلقة الرباعية



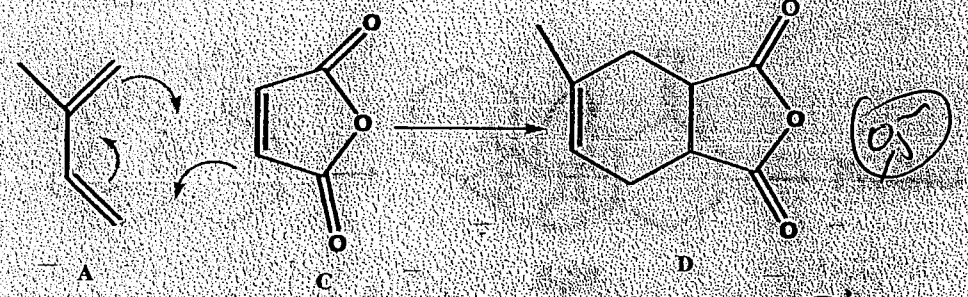
التفاعل الحرارى

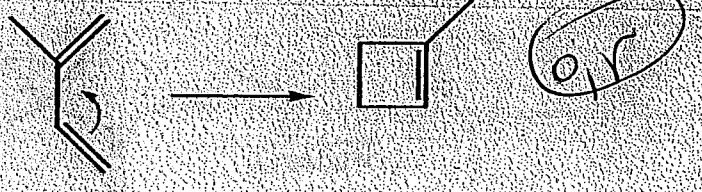
B ⟶ D

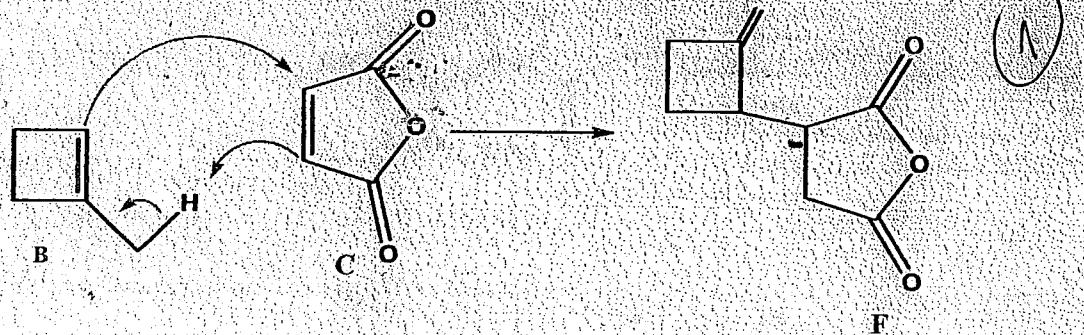
لوران متعاكس

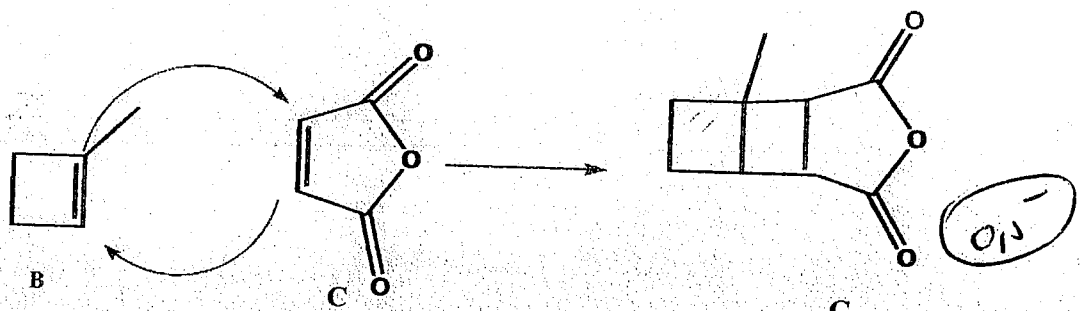


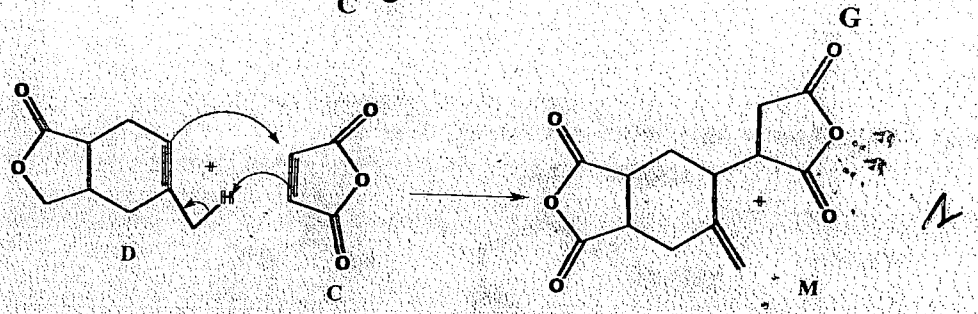
ب- آلية وتتفق هذه التفاعلات

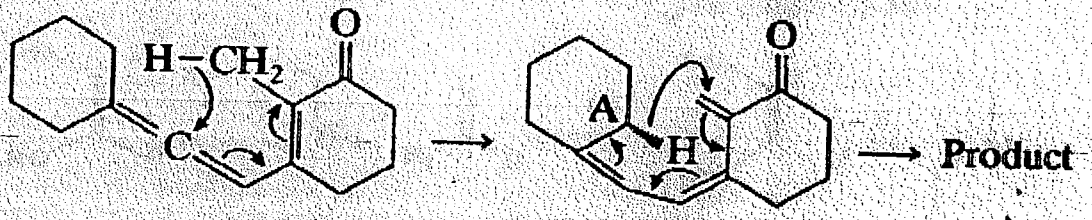






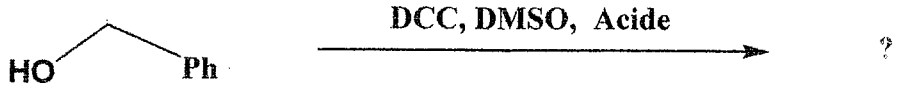


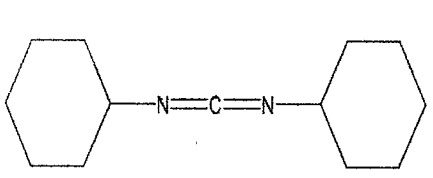




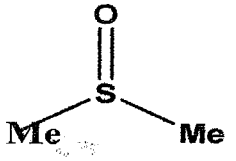
6-20

EXERCICE N°1 :
Donner le produit et le mécanisme de la réaction de Moffat ci-dessus :



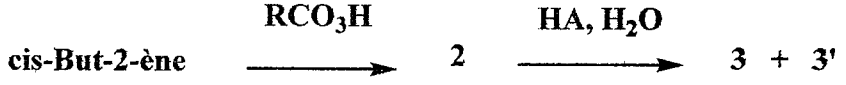


DCC : le dicyclohexylcarbodiimide



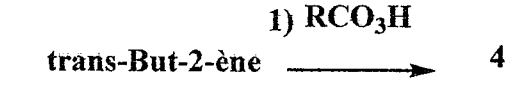
DMSO : Diméthylsulfoxyde

EXERCICE N°2 :
On effectue la transformation du composé 1 nommé selon l'UICPA cis-But-2-ène en un mélange de deux espèces selon le schéma suivant :



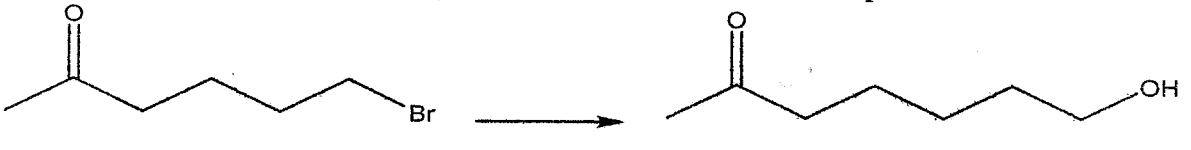
- Compléter le schéma ci-dessus en donnant les structures des produits **2, 3** et **3'**.
- Préciser la relation entre **3** et **3'**
- Déterminer les configurations absolues des atomes asymétriques des produits **3** et **3'**.

D'autre part, la transformation du trans-But-2-ène en **4** selon le schéma suivant :



- Donner la structure du produit **4**
- La molécule **4** est –elle chirale ?

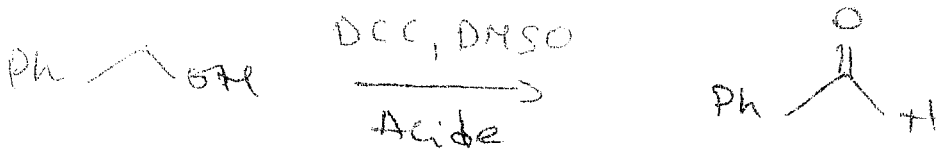
EXERCICE N°3:
Proposer un mécanisme commode permettant de transformer le composé A en B.



A B

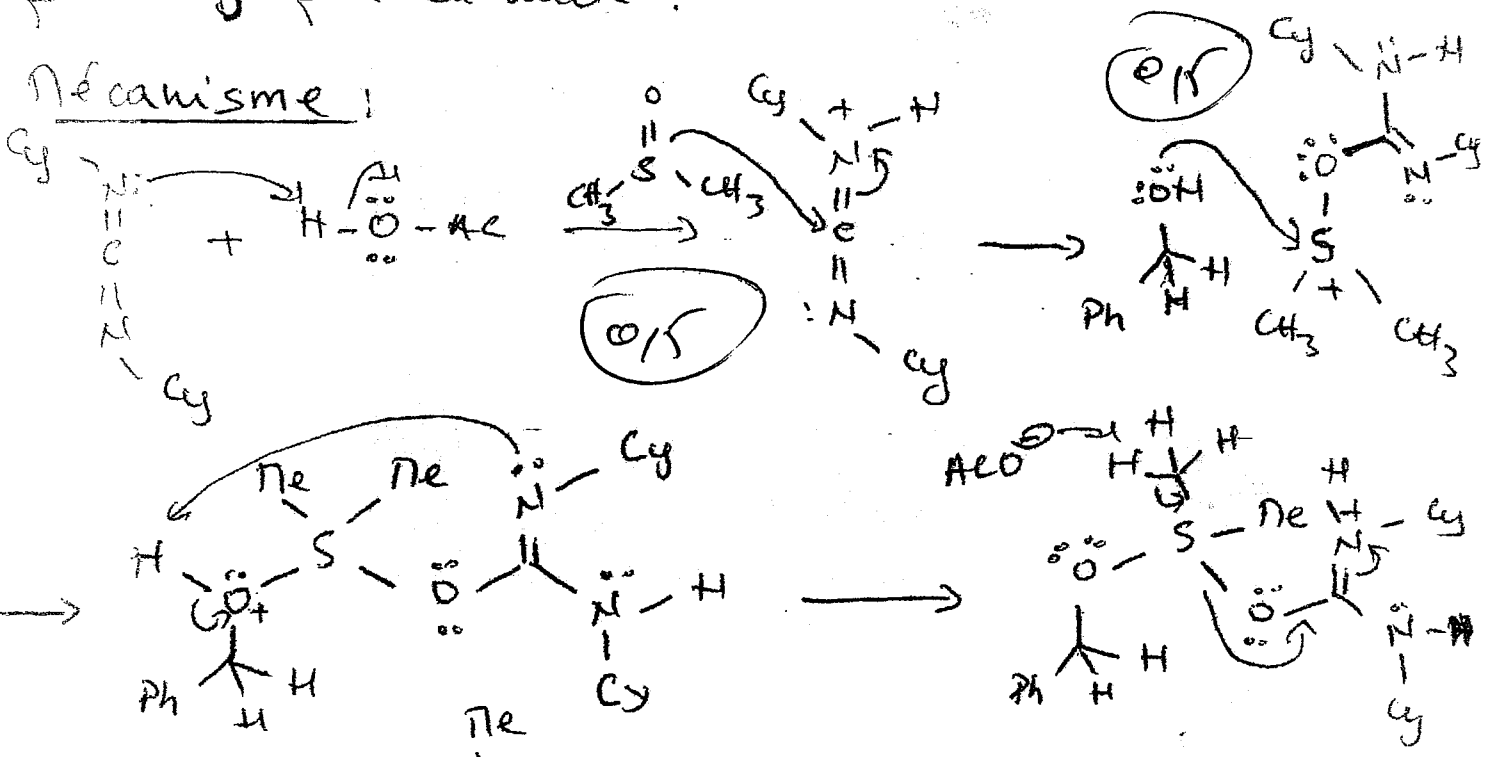
Problème:
Soit le composé **5** qui sert de produit de départ pour la synthèse de différents composés cycliques fonctionnalisés.

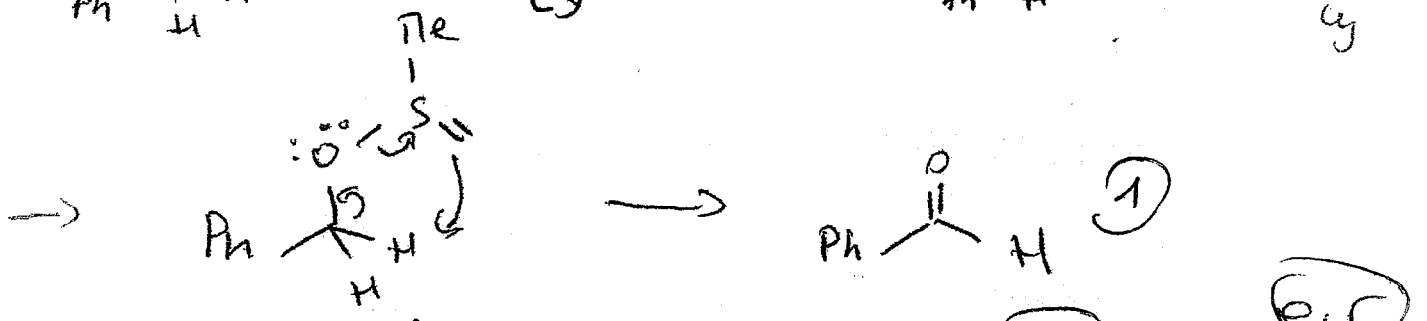
Exercice n°1 2pts



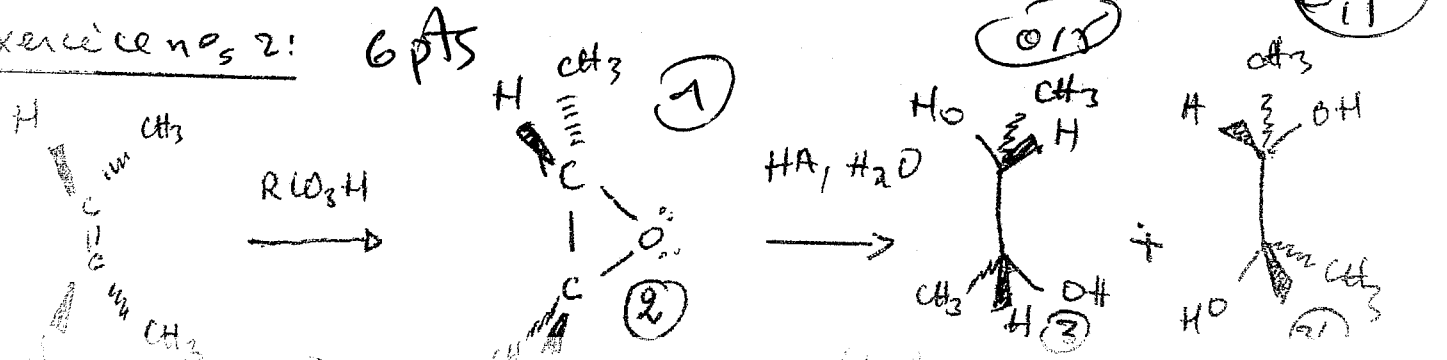
Un alcool primaire est oxydé en aldéhyde par le DMSO activé par le DCC et une quantité catalytique d'acide.

Mécanisme :

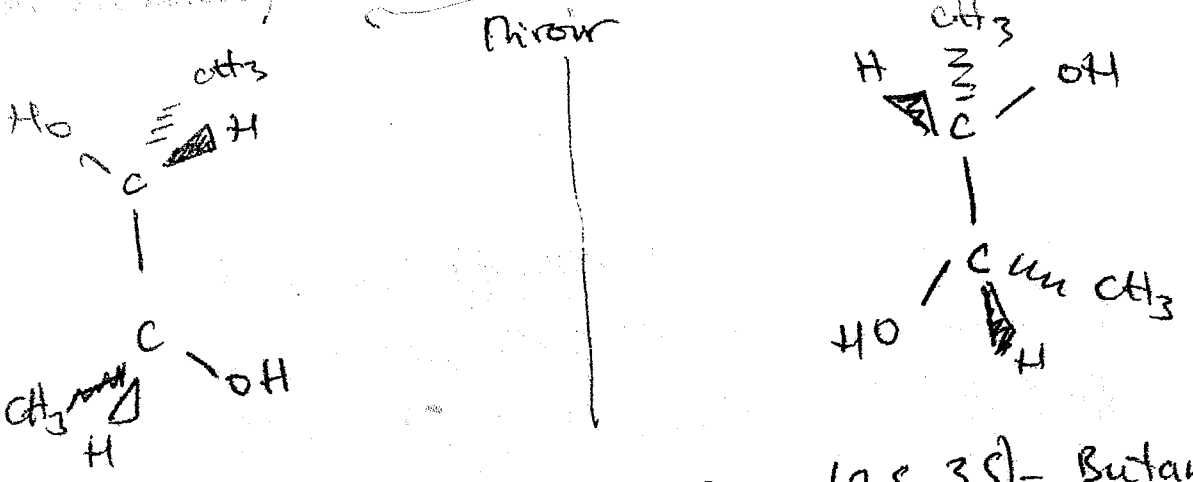




Exercice n°2 : 6pts

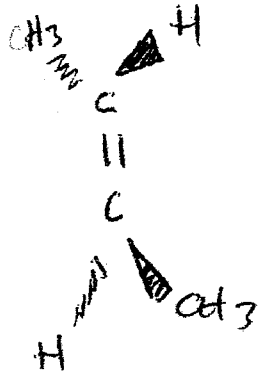


Une hydrolyse qui catalyse acide (une catalyse acide) 2 énantiomères du butane-2,3-diol.



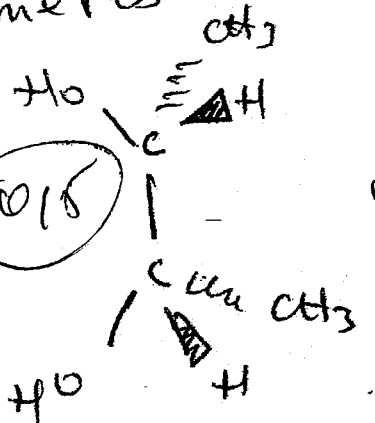
(2R, 3R)-Butane-2,3 diol ; (2S, 3S)-Butane-2,3-diol

Enantiomères



Trans-But-2-ène

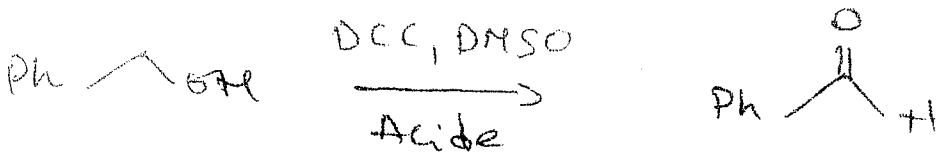
1) RCO_3H
2) HA, H_2O



méso Butane-2,3-diol

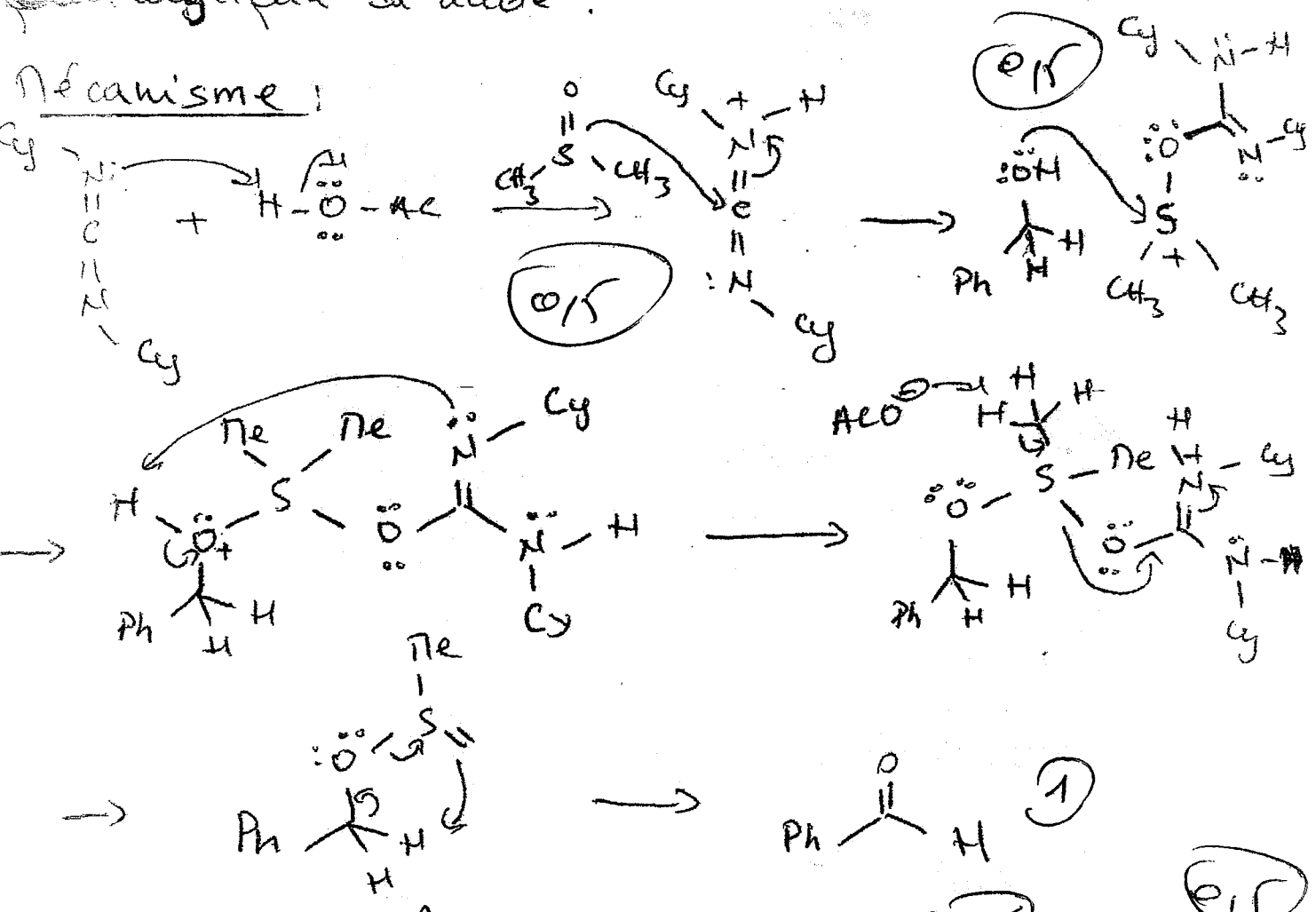
la molécule 4 est un composé Méso qui admet un plan de symétrie et donc la molécule n'est pas chirale.

Exercice n°s 1 2pts

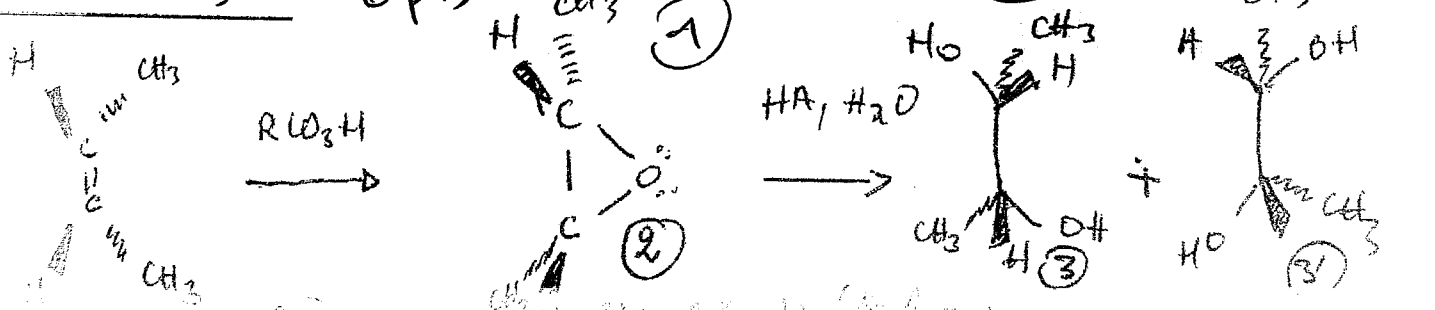


Un alcool primaire est oxydé en aldéhyde par le DMSO activé par le DCC et une quantité catalytique d'acide.

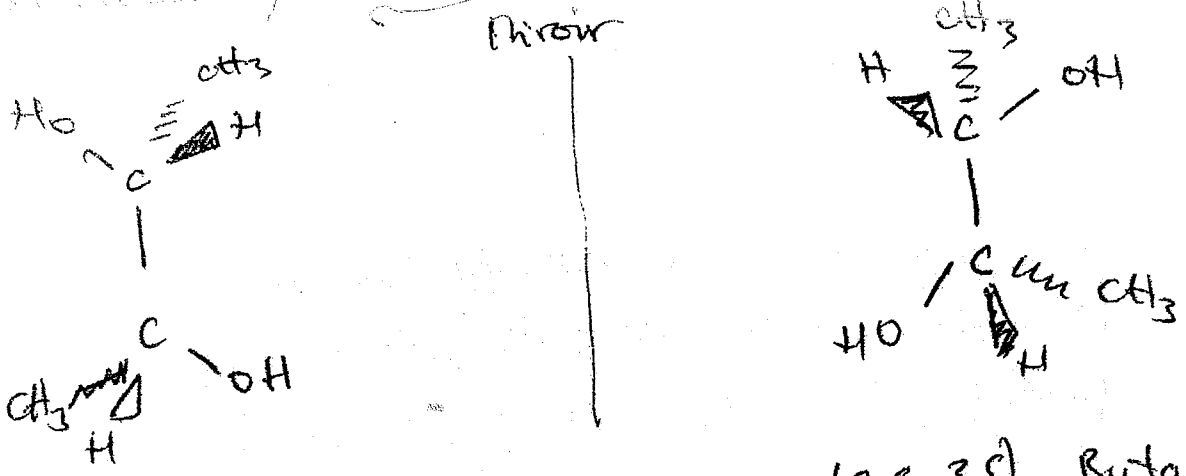
Mécanisme :



Exercice n°s 2 : 6pts



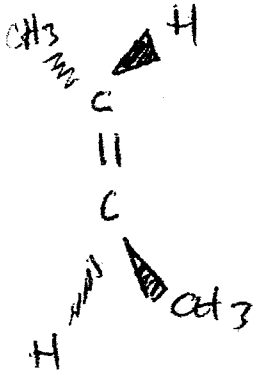
Hydrolyse par catalyse acide (acide de Lewis ou de Brønsted) 2 énantiomères du butane-2,3-diol.



(2R,3R)-Butane-2,3-diol ; (2S,3S)-Butane-2,3-diol

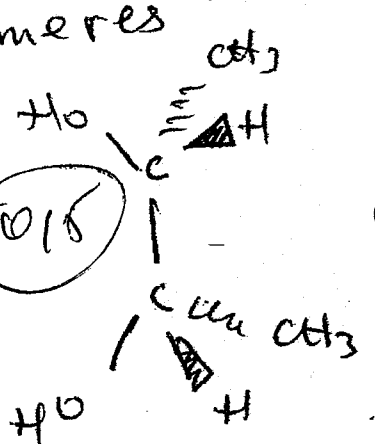
(0,5) (0,5)

Enantiomères



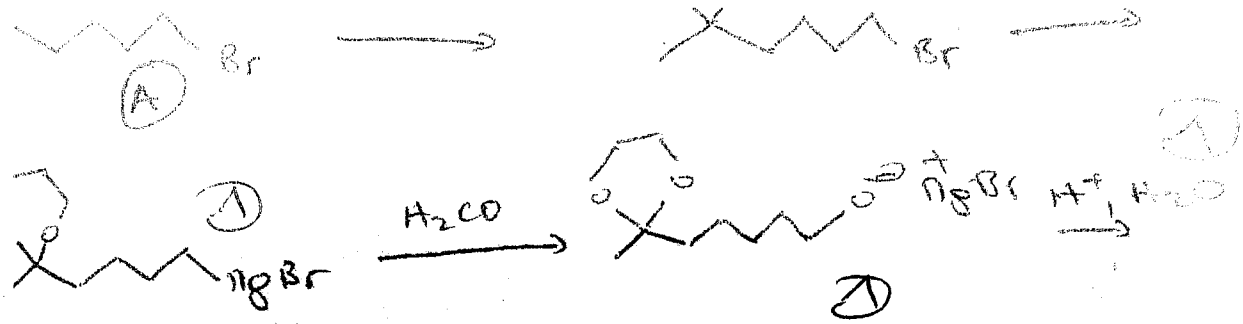
Trans-But-2-ène

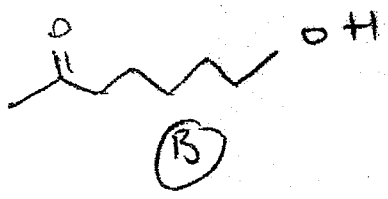
1) RCO_3H
2) HA, H_2O



(0,5) méso Butane-2,3-diol (4)

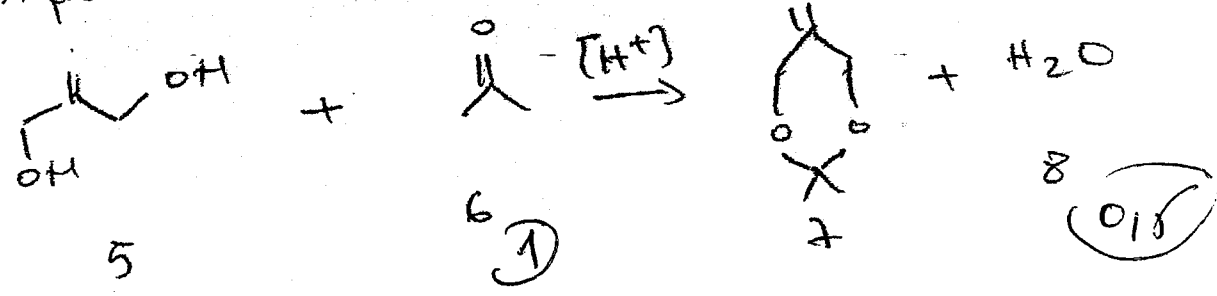
La molécule 4 est un composé Méso qui admet un plan de symétrie et donc la molécule n'est pas chirale. (1)



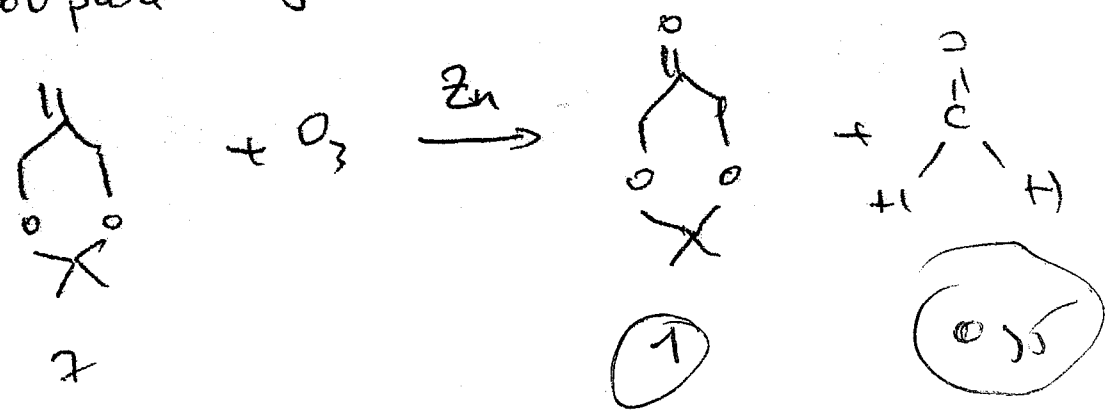


Problème 1 :

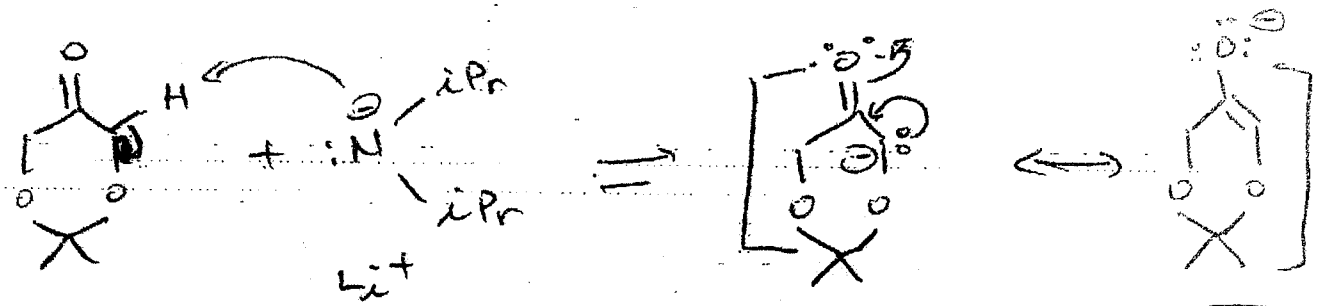
1 - Transformation 5 + 6 ⟶ 7 + 8 (réaction classique d'acétalisation).



2 - Réaction d'ozonolyse de 7 (Réaction classique de coupure oxydante d'un Alcène par l'ozone)



Structure limites de 12 : Le LDA (base forte) arrache un proton en α du carbonyle pour conduire à un carbanion stabilisé par résonance.



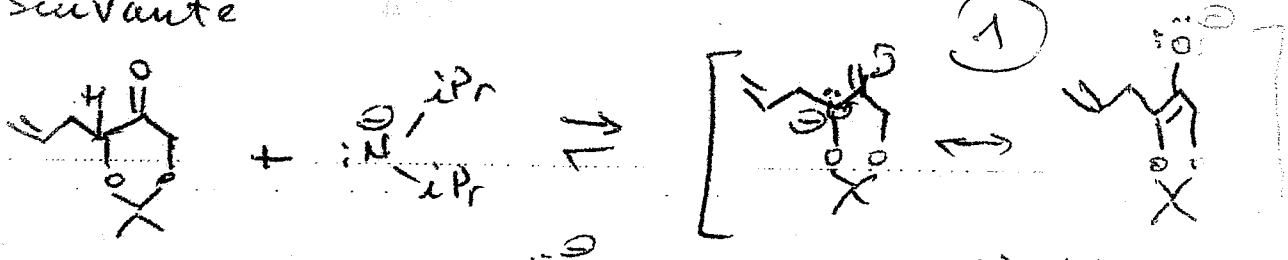
0,5 12 0,5

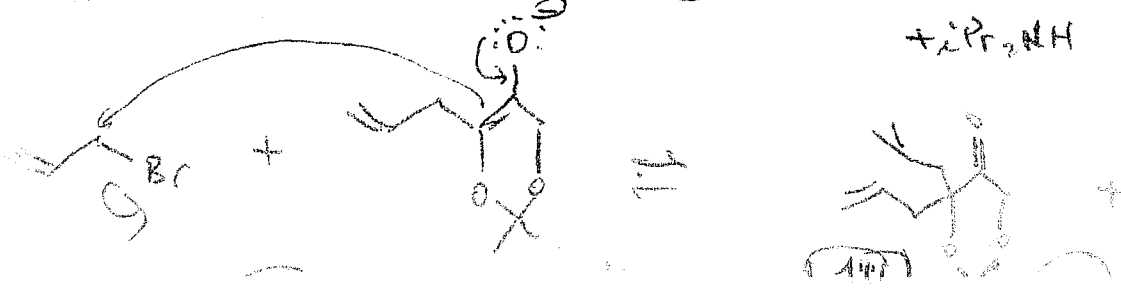
4 - contrôle Thermodynamique.

Le produit 13 (monoalkylé) est à nouveau déprotoné par le LDA - il y a maintenant deux types de protons en α du carbonyle susceptibles d'être arrachés par la base.

sous contrôle Thermodynamique, le produit formé ne contient pas d'atome de carbone asymétrique. On a donc formé l'enolate le plus substitué (le plus stable) qui conduit à 14 selon la réaction suivante

(1)





[illegible] Chemistry Department

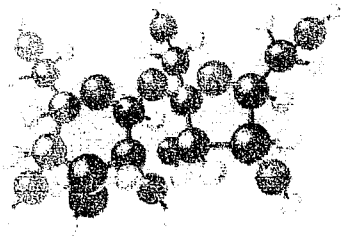
English Exam

[illegible] 1st Master

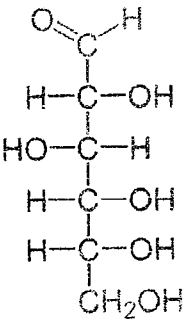
Time : 1h. 30m

Most living organisms contain 70% or more of water. The rest is mainly compounds of carbon, all acquired initially as carbon dioxide by plants during photosynthesis. Carbon has a valency of four and it can form large complex covalent molecules. These molecules contain carbon atoms linked together in rings and chains, together with oxygen, hydrogen and a few other elements. The study of carbon compounds is called organic chemistry. Living things contain three main groups of organic compounds: carbohydrates, lipids, proteins.

A....?..... contain carbon, hydrogen and oxygen only, and their molecules contain twice as many hydrogen atoms as oxygen atoms. Important carbohydrates include starch, sugars and cellulose. All green plants produce starch by photosynthesis. Starch is the energy store of the plant and has the formula $(C_6H_{10}O_5)_n$. The molecule consists of a large number (n) of identical units linked together in various ways. Starch is easily broken down in plants, and in the digestive systems of animals, into simple sugars including sucrose (cane sugar - $C_{12}H_{22}O_{11}$) and glucose (blood sugar -$C_6H_{12}O_6$). Enzymes in the digestive system convert sucrose and water into simpler sugars like glucose.



C ....?.....



D....?.....

$C_{12}H_{22}O_{11} + H_2O \longrightarrow$ B ...?.....

Cellulose $(C_6H_{10}O_5)_n$ has the same formula as starch but a different structure. It consists of a few hundred to a few thousand glucose units firmly linked together in long, straight chains (as shown in the illustration below). Substances like this, with molecules that are long chains of repeating units, are called *polymers*. Cellulose is the most abundant of all organic compounds. It forms the cell walls in plant cells, including the walls of the xylem and phloem vessels, and it is a major constituent of wood. Because it is a polymer, cellulose is fibrous. The digestive system does not easily break it down, so cellulose provides the fibrous bulk needed for our faeces. In industry, we use cellulose (in the form of wood pulp and cotton pulp) to make paper and fibreboard. We also use it to produce plastics including cellophane for wrapping and cellulose acetate for making films and the frames of spectacles.

E....?..... are oils (liquid) and fats (solid), and they contain carbon, hydrogen and oxygen only. The molecules are complex with most of the carbon atoms linked together in chains. Lipids provide stores of energy in plants and animals and are part of the structure of cell membranes. They are an important part of our diet and we use them in many ways when we prepare food. We use plant oils like canola, palm and coconut for heating (frying) food while others, like olive and sesame oils, provide flavour or carry the flavour of other foods such as spices and herbs. We use butter and other lipids to alter the texture and flavour of food. Most plant and fish oils are *polyunsaturated*. This means that many of the carbon atoms in their molecules are joined by *double bonds* (bonds where *two* pairs of electrons are shared - like those between C and O in CO_2 -). These oils are an important part of a healthy diet, but eating a lot of *saturated* fats, such as butter and other animal fats (which have no double bonds) is associated with heart disease. In addition to food, we use lipids to make soap, candles, perfumes and cosmetics.

E ....?..... contain nitrogen as well as carbon, hydrogen and oxygen. They are complex polymers of *amino acids* linked together into long chains. The structure of an amino acid is shown on(Q_3). R is a variable radical based on a chain of carbon atoms of the amino acid. Proteins are the main components of living cells and (after water) they are the commonest molecules in the human body. Our bodies need proteins for growth and maintenance. We get proteins when we eat meat, fish, milk, eggs, grains and vegetables. They are key nutrients for success in sport! When we digest proteins, amino acids are released and used to build new tissue (including muscle) and to repair damaged tissue.

Questions

1- Give a title to this text.**(2 pts)**

2- Fill the gaps (A B C D E). **(2.5pts)**

3- Draw the structure of each of the amino acid and the peptide bond. **(3pts)**

4- What characterizes a protein from each other? **(2pts)**

5- For what do our bodies use each of the following: (i) glucose, (ii) cellulose, (iii) lipids, (iv) proteins ? **(2pts)**

6-List the industrial uses of (i) cellulose, (ii) lipids. **(2pts)**

7-Explain the following terms: (i) polymer, (ii) lipid, (iii) double bond, (iv) saturated fats, (v) amino acid. **(2.5pts)**

8- Why do starch and cellulose behave differently? **(2. pts)**

9 – Write the definitions and then mention examples from text for following:
noun, verb, adjective, adverb. **(2. pts)**

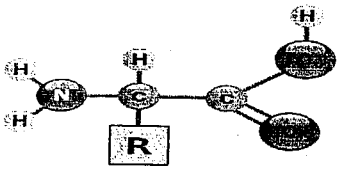
1er

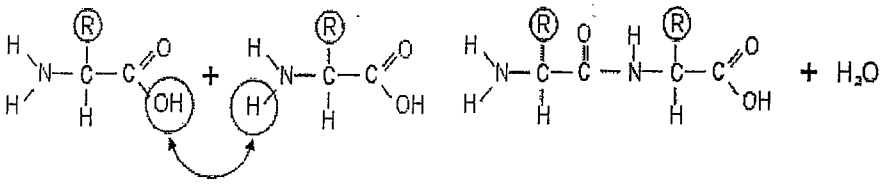
Master corrction

1- title to this text **CARBON – THE ELEMENT OF LIFE** .

2- Fill the gaps (A= (**Carbohydrates**) . B($2C_6H_{12}O_6$) . C (Model of **sucrose**) .D (***Glucose***) .E(**Lipids**) .).

3- the structure of each of the amino acid and protein.





4- Characterizes a protein from each other are the types and ranking (classification)of amino acids

5-. Our bodies need ... **(i)** ... glucose as a source of energy through respiration. **(ii)** ... cellulose for fibre to provide bulk for our faeces. **(iii)** ... lipids for storing energy and for constructing cell membranes. **(iv)** ... proteins for growth of tissues and the repair of damaged tissues.

6-(i) Cellulose is used for making paper, fibreboard and plastics such as cellophane and cellulose acetate. (ii) Lipids are used in preparing foods, and in making soap, candles, perfumes and cosmetics

7-(i) A polymer is a compound with molecules that consist of long chains of repeating units. (ii) A lipid is an oil or fat found in, or obtained from, a living organism.. (iii) A double bond is a covalent bond in which *two* pairs of electrons are shared between two atoms. (iv) Saturated fats are fats whose molecules do not contain double bonds between carbon atoms. (v) An amino acid is a compound with the following formula/structure (in which R represents a radical based on a chain of carbon atoms). $C_2H_4O_2NR$ – often partly expanded as $NH_2CHRCOOH$, or more fully as illustrated:

8- Starch and cellulose have the same formulae, but they behave differently because they have different structures. In starch the glucose units are linked in a variety of different ways and the links are easily broken down. In cellulose the glucose units are firmly linked into long straight chains that are very hard to break down.

9 – Write the definitions and then mention examples from text for following: noun, verb, adjective, adverb

-A noun is the name of a person, place, thing, or idea. Whatever exists, we assume, can be named, and that name is a noun.

- **Verbs** carry the idea of being or action in the sentence.

-**Adjective**: simply put adjectives are descriptive words. Adjectives are used to describe or give information about things, ideas and people: nouns or pronouns.

- **Adverbs** can tell you where, when, how, why and to what extent something happens.

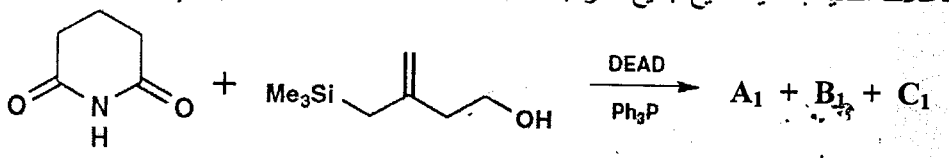
There are several different classes of adverb.

Université Hamma lakhdar-Eloued
Faculté des Sciences exactes
Département de Chimie

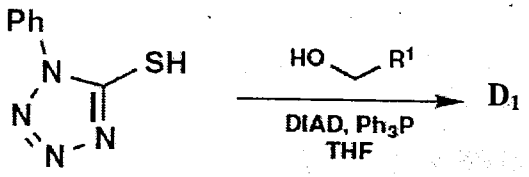
Examen de Stratégie de Synthèse

Le 08/01/2017 Durée : 1h30

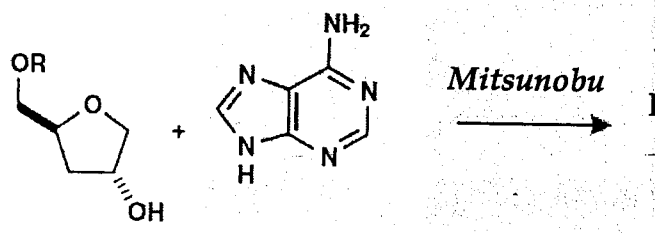
Exercice 1 : (09.00 pts) أكمل سلسلة التفاعلات التالية بتحديد صيغ جميع المركبات

1) 

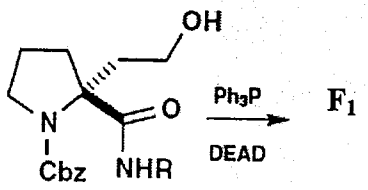
$A_1 + B_1 + C_1$

2) 

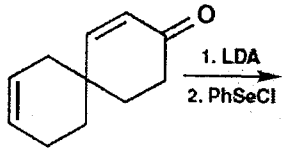
D_1

3) 

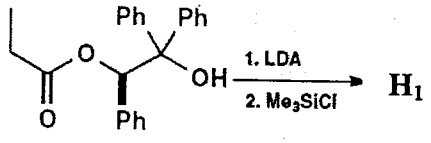
E_1

4) 

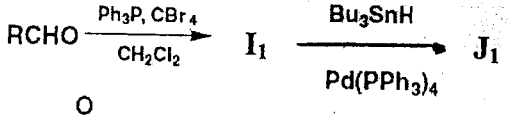
F_1

5) 

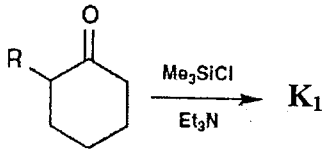
G_1

6) 

H_1

7) 

I_1 J_1

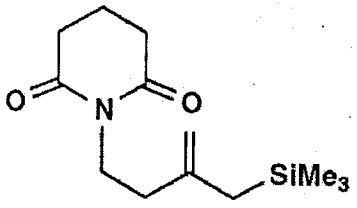
8) 

K_1

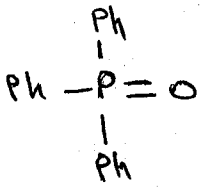
التصحيـــح النموذجي

Stratégie de Synthèse 2016-2017

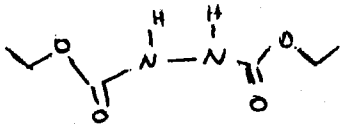
Exercice 1 **: (*9.00 pts*)**



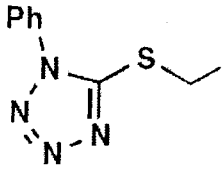
A_1 *(1.00)*



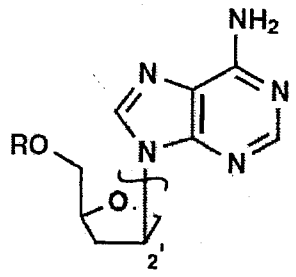
B_1 **(0.50)**



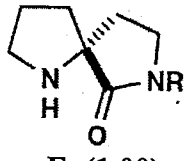
C_1 **(0.50)**



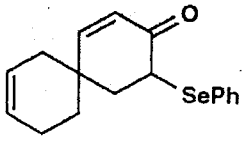
D_1 *(1.00)*



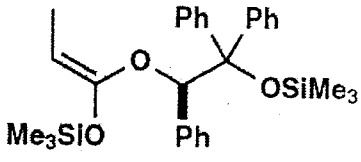
E_1 *(1.00)*



F_1 **(1.00)**

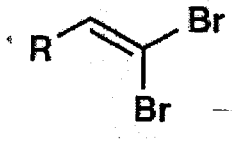


G_1 **(1.00)**

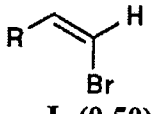


H_1 **(1.00)**

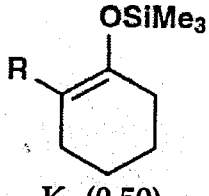
3)



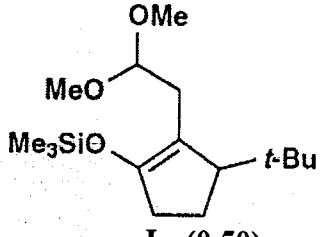
I_1 *(0.50)*



J_1 **(0.50)**

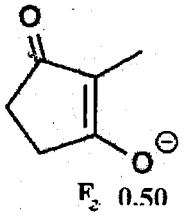


K_1 **(0.50)**

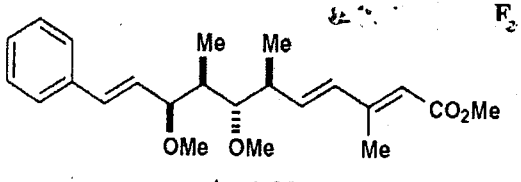


L_1 **(0.50)**

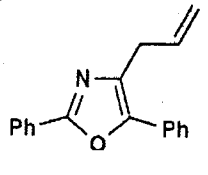
Exercice 2 **: (*07.00 pts*)**



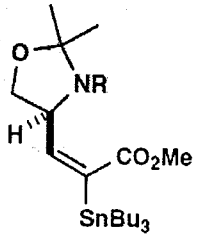
F_2 0.50



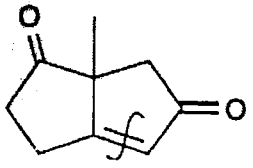
A_2 1.00



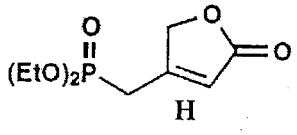
B_2 1.00



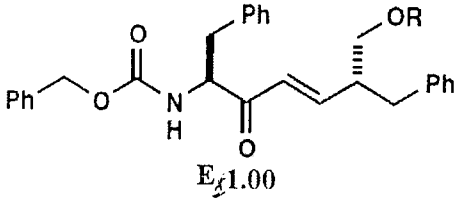
1.00 C_2



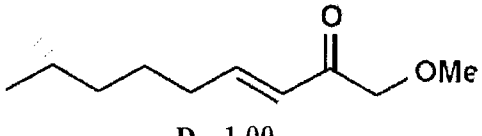
G_2 1.00



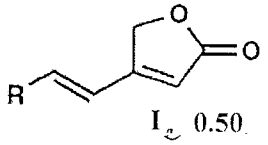
H



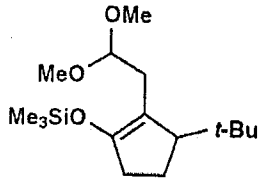
E_2 1.00



D_2 1.00

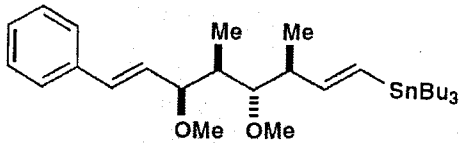


I_2 0.50

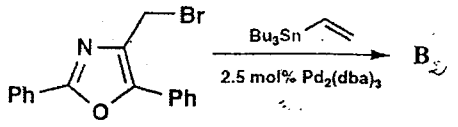
9) 

$\rightarrow$ L_1

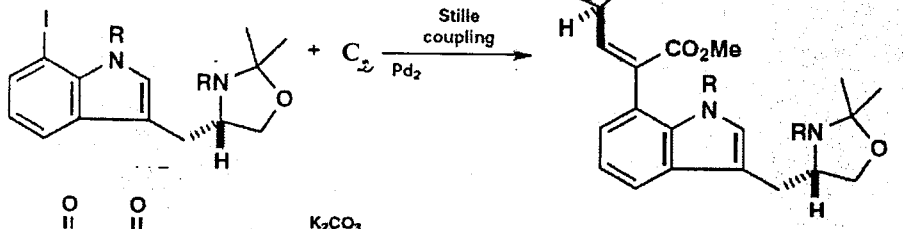
Exercice 3 : (*7.00 pts*) أكمل سلسلة التفاعلات التالية بتحديد صيغ جميع المركبات

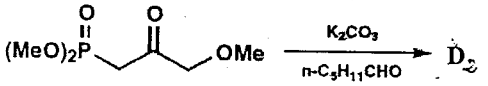
1) 

A_2

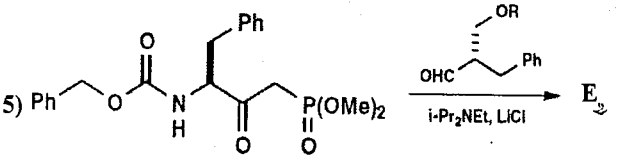
2) 

B_2

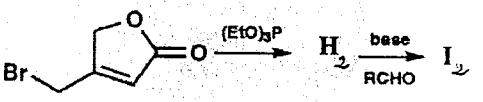
3) 

4) 

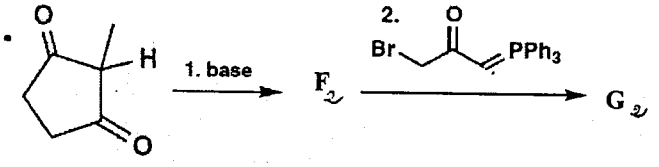
D_2

5) 

E_2

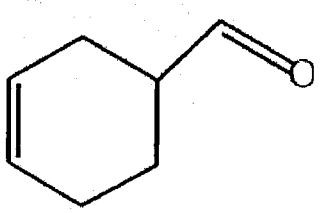
7) 

I_2

6) 

F_2 G_2

Exercice 1 : (*04.00 pts*): حدد جميع المركبات C_3, B_3, A_3



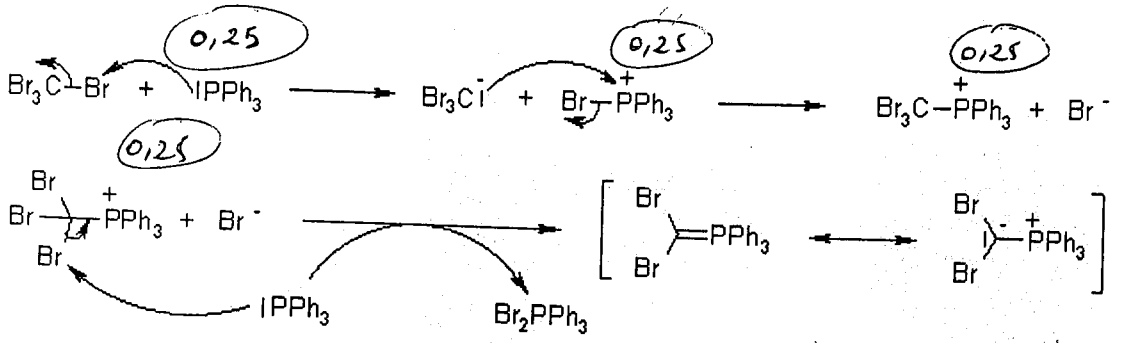
$PPh_3/CBr_4/Zn$

mécanisme ?

A_3 $\rightarrow$ B_3 $\xrightarrow{2\ n\text{-BuLi}}$ C_3

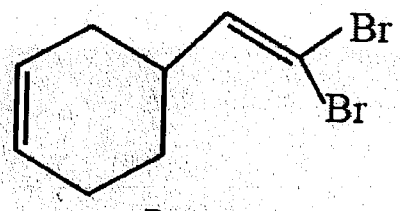
Good Luck

Exercice 3 : *(4.00 pts)*

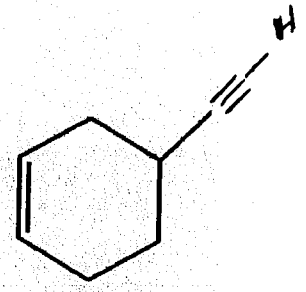


$Ph_3P{=}CBr_2$

A_3 (1.00)



B_3 (1.00)



C_3 (1.00)

Université Echahid Hamma Lakhdar. El-Oued

Institut des Sciences exactes
Master chimie
Le 05 /01 /2017

Matière : Chimie analytique des réactions couplées
Durée : 1h et 30m

Contrôle

Exercice 01(12 points): diagramme E-pH.

On se propose d'étudier le pouvoir oxydant du chrome (VI) en fonction du pH.

1-Tracer le diagramme E-pH du chrome dans les états d'oxydation VI, III, II et 0 entre les espèces suivantes : solides : Cr , $Cr(OH)_2$, $Cr(OH)_3$ espèces en solution (1 mol.L^{-1}): $Cr_2O_7^{2-}, Cr^{3+}, Cr^{2+}$.

2-Sur le même plan tracer E_1 = f(pH) pour le couple(I_2/ I^-) et E_2 = f(pH) pour le couple (Br_2/ Br^-).

3- Montrer qu'il est possible d'oxyder les ions iodure sans oxyder les ions bromure en utilisant l'oxydant Cr(VI).

On donne :

E° $(Cr_2O_7^{-2}/Cr^{3+})$ = 1,33 V E° $(Cr^{3+}/Cr^{2+}) = -0{,}41\,V$, E° $(Cr^{2+}/Cr) = -0{,}91\,V$, pKs$_1$ $(Cr(OH)_3)$ = 30 pKs$_2$ $(Cr(OH)_2)$ = 17, E° (I_2/I^-) = $0.62\,V$, E° $(Br_2/Br^-) = 1.10\,V$.

Exercice 02 (08 points): diagramme E-pL.

Les ions cobalt (II) Co^{+2} et cobalt (III) Co^{+3} donnent avec l'ammoniac NH_3, les ions complexes; $[Co(NH_3)_6]^{+3}$, $[Co(NH_3)_6]^{+2}$.

On demande de tracer le diagramme E-pL (E-pNH_3) du cobalt pour une concentration de tracé égale à 0,01 mol/l.

On donne : E° $(Co^{3+}/Co^{2+}) = 1.81\,V$, E° $(Co^{2+}/Co_{(S)}) = -0{,}28\,V$,

$$pKc[Co(NH_3)_6]^{+3} = 34.8\,,pKc[Co(NH_3)_6]^{+2} = 4.2$$

Solution d'examen 2017

Exercice : (01)

1- Diagramme E-pH du chrome :

$Cr(VI) : Cr_2O_7^{-2}$, $Cr(III) : Cr^{+3}$, $Cr(OH)_3$

$Cr(II) : Cr^{+2}$

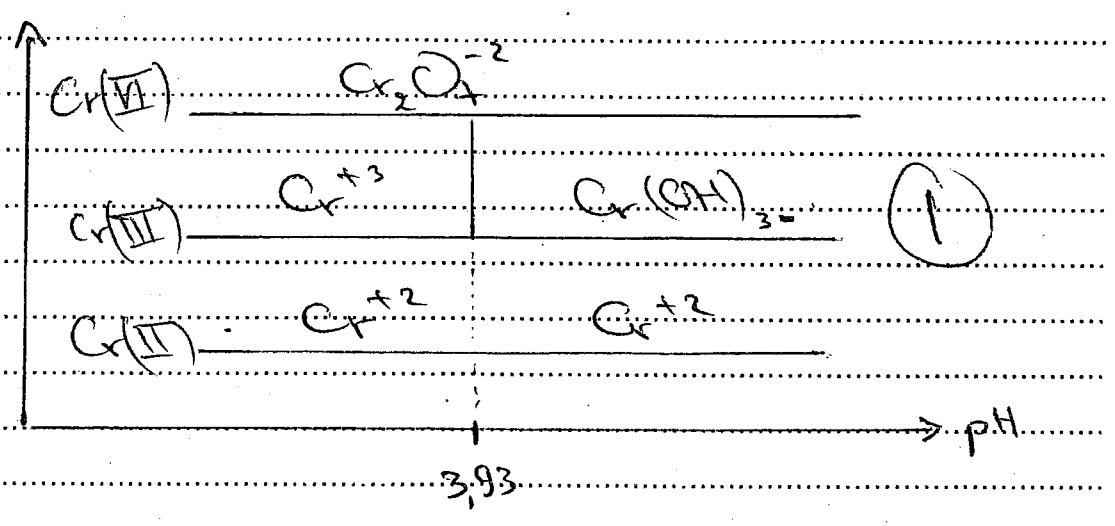
* Calcul du pH frontière pour $Cr(OH)_3$

On a : $Cr(OH)_{3(s)} \rightleftharpoons Cr^{+3} + 3OH^-$

$K_s = [Cr^{+3}][OH^-]^3 \Rightarrow [OH^-] = \sqrt[3]{\frac{K_s}{[Cr^{+3}]}}$

$[OH^-] = \frac{K_e}{[H_3O^+]} \Rightarrow [H_3O^+] = \frac{K_e}{[OH^-]} = \frac{K_e}{\sqrt[3]{\frac{K_s}{[Cr^{+3}]}}}$

$\Rightarrow \boxed{pH = 3,93}$ (1)



(1)

a) Frontière (A) : à $pH < 3,93$ le couple $(Cr_2O_7^{-2} / Cr^{+3})$

$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{+3} + 7H_2O$

(1)

$E_A = E_{0A} + \frac{0,06}{6} \log \frac{[Cr_2O_7^{-2}][H^+]^{14}}{[Cr^{+3}]^2}$ ⇒ (1)

$E_A = 1,33 + 0,14 \log [H^+]$ ⇒ $\boxed{E_A = 1,33 + 0,14\ pH}$ (1)

b) Frontière (B) à $pH > 3,93$ le couple $(Cr_2O_7^{-2} / Cr(OH)_3)$

$Cr_2O_7^{-2} + 8H^+ + 6e^- \rightleftharpoons 2Cr(OH)_3 + H_2O$

$\boxed{E_B = 1,094 - 0,08\ pH}$ (2) (1)

c) Frontière (C) : à $pH < 3,93$ le couple (Cr^{+3} / Cr^{+2})

$Cr^{+3} + 1e^- \rightleftharpoons Cr^{+2}$

$\boxed{E_C = E_{0C} = -0,41\ V}$ (3) (1)

d) Frontière (D) : à $pH > 3,93$ le couple $(Cr(OH)_3 / Cr^{+2})$

$Cr(OH)_3 + 3H^+ + 1e^- \rightleftharpoons Cr^{+2} + 3H_2O$ (1)

$E_D = E_{0D} - 0,18\ pH$ ⇒ $\boxed{E_D = 0,297 - 0,18\ pH}$ (4)

2 - * $E_1 = f(pH)$ pour (I_2 / I^-)

$I_2 + 2e^- \rightleftharpoons 2I^-$

$E_1 = E_{01} + \frac{0,06}{2} \log \frac{[I_2]}{[I^-]}$ ⇒

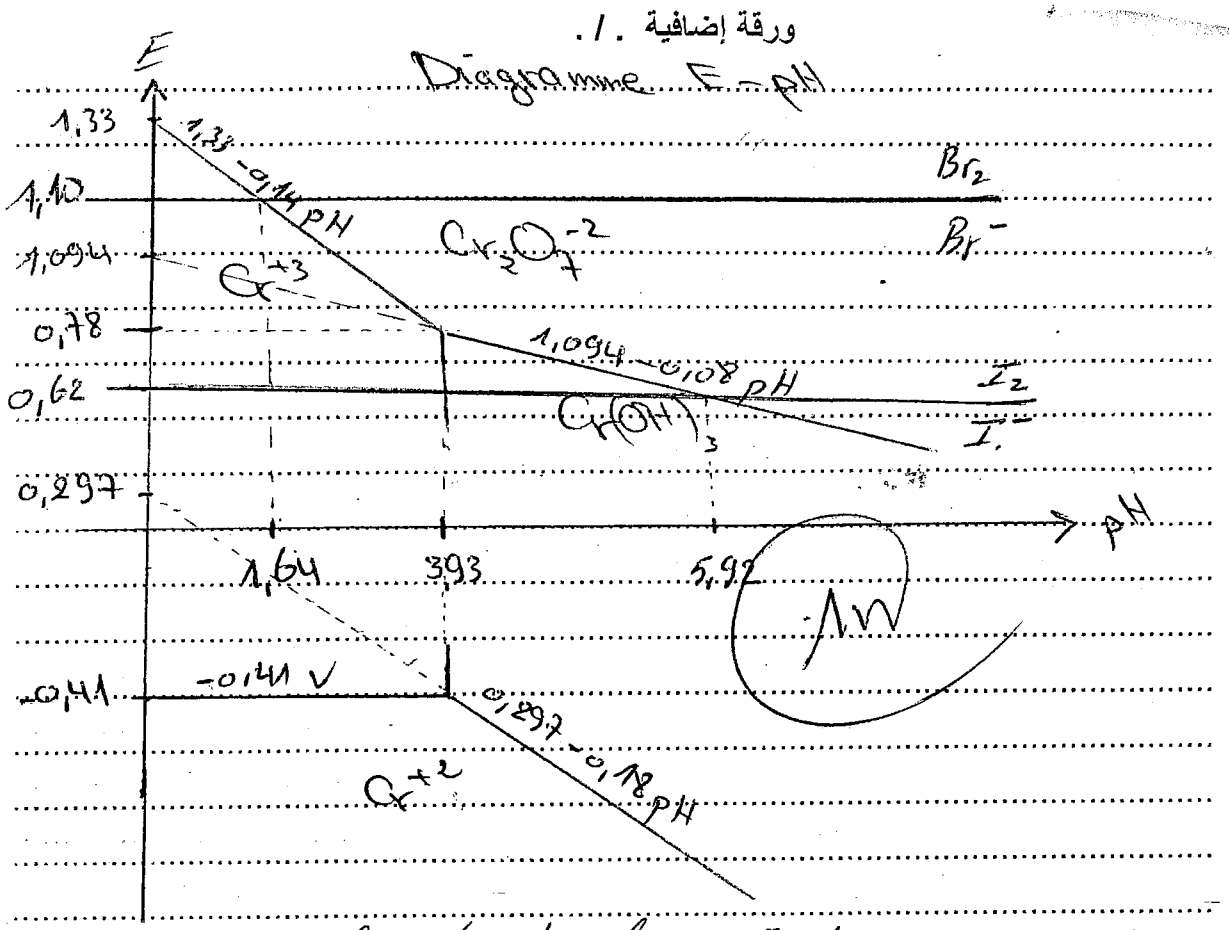
$\boxed{E_1 = E_{01} = 0,62\ V}$ (5) (1)

* $E_2 = f(pH)$ pour (Br_2 / Br^-) (1)

$Br_2 + 2e^- \rightleftharpoons Br^-$ ⇒ $\boxed{E_2 = E_{02} = 1,10\ V}$ (6)

ورقة إضافية . 1 .

Diagramme E – pH



3- Il est possible d'oxyder les ions iodure sans oxyder les ions bromure en utilisant l'oxydant Cr(VI). (1)

$1,10 = 1,33 - 0,14\ pH \Rightarrow pH = 1,64$

Les ions Br^- peuvent être oxydés en Br_2 si $pH < 1,64$ par l'ion dichromate.

$0,62 = 1,094 - 0,08\ pH$ donne $pH = 5,92$

Les ions I^- peuvent être oxydés en I_2 si $pH < 5,92$ (1) par l'ion dichromate.

On peut oxyder I^- sans oxyder Br^- dans l'intervalle de pH : $]1,64 ; 5,92[$.

$1,64 < pH < 5,92$ (0,5)

Exercice (06.):

Diagramme E – pL du cobalt

1) pL de dissociation de $[Co(NH_3)_6]^{+3}$.

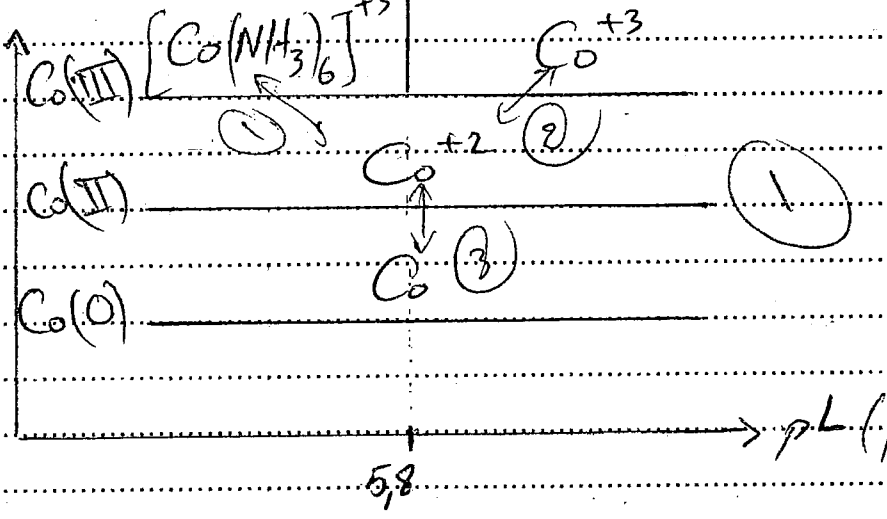
$$[Co(NH_3)_6]^{+3} \rightleftharpoons Co^{+3} + 6NH_3$$

$$K_C = \frac{[Co^{+3}][NH_3]^6}{[Co(NH_3)_6]^{+3}} \Rightarrow K_C = [NH_3]^6$$ (O.K)

$$\Rightarrow [NH_3] = \sqrt[6]{K_C} = [K_C]^{1/6}$$

$$\Rightarrow pNH_3 = \frac{pK_C}{6} = \frac{34,8}{6} = 5,8$$ (1)

donc :



2) Frontière (1) le couple $([Co(NH_3)_6]^{+3} / Co^{+2})$ à $pL < 5,8$

$$[Co(NH_3)_6]^{+3} + 1\,e^- \rightleftharpoons Co^{+2} + 6NH_3$$ (0.K)

$$E_1 = E_{0,1} + 0,06 \log \frac{[[Co(NH_3)_6]^{+2}]^{+3}}{[Co^{+3}][NH_3]^6}$$ (1)

$$E_1 = E_{0,1} + 0,36\,pL \quad \cdots (1)$$

$$E_1 = -0,298 + 0,36\,pL$$ (1)

(4)

ورقة إضافية .1.

3.) Frontière (2) : le couple (Co^{+3}/Co^{+2}) à pL > 5,8

$Co^{+3} + 1\acute{e} \leftrightharpoons Co^{+2}$

$\boxed{E_2 = E°_2 = 1,81\ V}$ --- (2)

4.) Frontière (3) : le couple (Co^{+2}/Co)

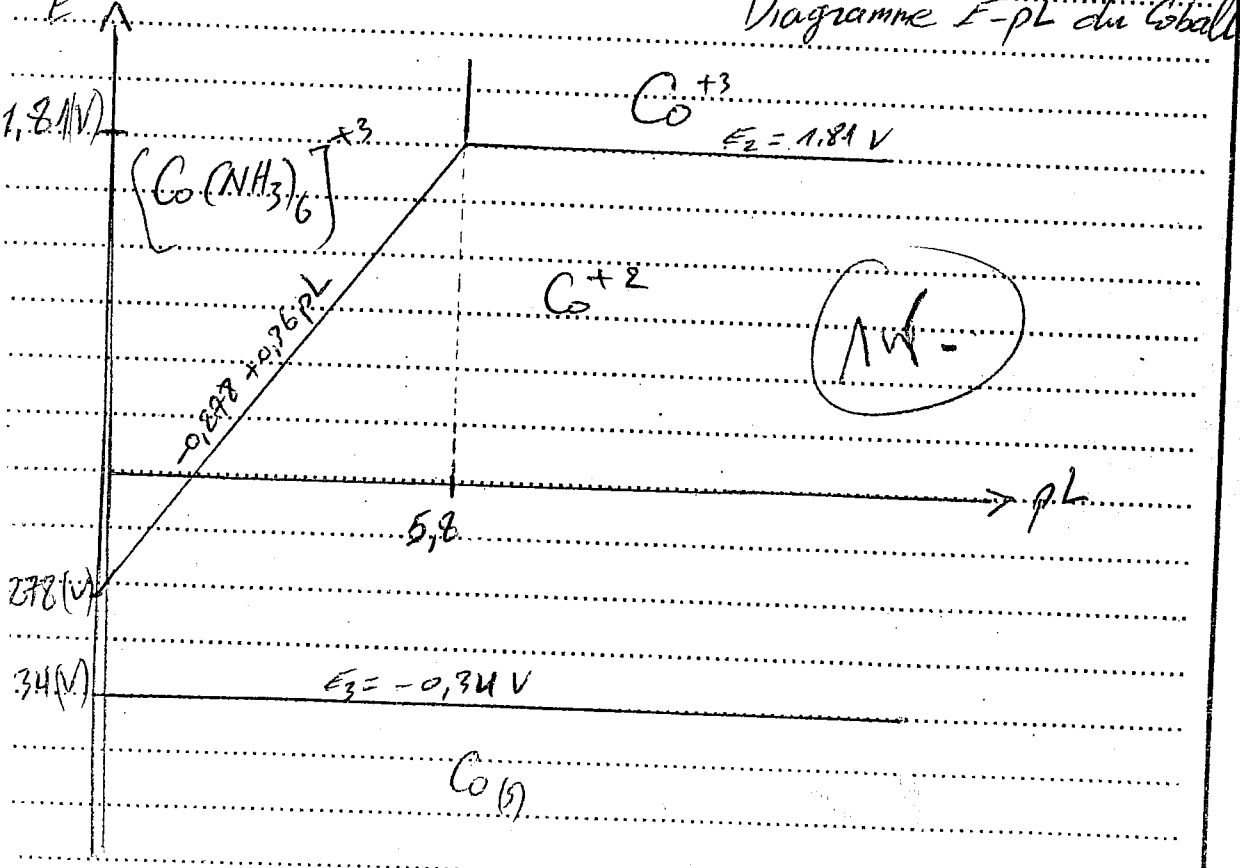
$Co^{+2} + 2\acute{e} \leftrightharpoons Co$

$E_3 = E°_3 + \frac{0,06}{2} \log \frac{[Co^{+2}]}{[Co]}$ on

$E_3 = -0,28 + 0,03 \log 10^{-2} = -0,34\ V$

$\boxed{E_3 = -0,34\ V}$ --- (3)

Diagramme E-pL du Cobalt



Université Hamma Lakhdar El-Oued — Année Universitaire 2016/2017

Faculté des Sciences Exactes — 1éré Année Mastère, Durée 1.5 h

Contrôle : informatique pour la chimie

Exercice N°1(08pts) Les instructions et les calculs matriciel a l'aide de Matlab.

1- **a)** - Que signifient les instructions suivantes. » **polyval(p,m),**

» **mod(a,b)** , » **sign(x)** , » **abs(z)** , » **horner(f)** » **compose(f,g)**, » **hold on** .

- Quell est la diffirence entre (» **legnth(A)** et » **size(A)**)

b) Soit les polynômes suivants :

$$a(x) = x^4-2x^3+11 \quad , \quad b(x)= x^2-2x+15.$$

1- Créer deux vecteurs pour représenter les polynômes (sur Matlab)

2-Quelle est l'instruction qui nous permettant de calculer le dérivé de q(x) qui est le produit **a(x)b(x).**

3-donner le résultat de calcul (manuellement) de ce dérivé.

2- Soit la matrice suivante. A=

47	58	69	80	1	12
57	68	79	9	11	22
67	78	8	10	21	32
77	7	18	20	31	42
6	17	19	30	41	52
16	27	29	40	51	62

Donnez les instructions qui nous permettant de :

a) Nommez et écrivez la matrice **D** a partir de matrice A, tel que **D** contienne dans la 1^{ére} ligne les éléments des positions suivantes **(5 ,8,13 ,20,26,32)** dans la 2^{éme} ligne **(4,10,17,23,31,36)** dans la 3^{éme} ligne **(36 ,11, 18,22, 6,19)** et la 4^{éme} ligne **(30 ,7, 10,27, 16 ,29)**.

b) Ajouter les six nombres suivants **8, 9 ,10 ,11 3 2** sur la **6^{éme}** ligne.(donnez la forme de la nouvelle matrice)

c) Donnez les significations et les résultats de calculs des ordres suivants. **A(2,6)= 10 , A(: , 3)= 12**

Exercice N°2 (05pts)

Ecrire le programme Matlab qui permet de créer les tracés des quatre fonctions **sin(k pi x)** pour **x** entre [0, 401] le pas est 1 et k = 1, 2, 3, 4 dans une figure en utilisant les ordres **grid on ,subplot** et les titres **title('k = 1'), title('k = 2') , title('k = 3') , title('k = 4').**

Exercice N°3 (07pts)

1- Définir une matrice $\mathbf{a} = \begin{pmatrix} 1 & 2 & 3 & 5 & 9 \\ 4 & 5 & 6 & 8 & 7 \\ 7 & 8 & 9 & 6 & 4 \\ 9 & 3 & 1 & 0 & 6 \\ 5 & 6 & 7 & 8 & 1 \end{pmatrix}$

Ecrire les commandes matlab permettant de :

1. Calculer la matrice transposée de **a** (donnez le résultat d'application)
2. Extraire les éléments de la diagonale de **a.** (donnez le résultat d'application)
3. Supprimer la première colonne de **a** (donnez le résultat d'application)
4. Supprimer la première ligne de **a**(donnez le résultat d'application)
5. Extraire la sous-matrice obtenue par suppression de la seconde ligne et de la seconde colonne de **a.**

2- b- On veux construire la matrice 4x4 en utilisant la boucle for –end , tel que $A(i, k)=i^2+k^2$.

Bon courage

c) Donnez les significations et les résultats de calculs des ordres suivants. **A(2,6)= 10 , A(: , 3)= 12**

Exercice N°2 (05pts)

Ecrire le programme Matlab qui permet de créer les tracés des quatre fonctions **sin(k pi x)** pour **x** entre [0, 401] le pas est 1 et k = 1, 2, 3, 4 dans une figure en utilisant les ordres **grid on ,subplot** et les titres **title('k = 1'), title('k = 2') , title('k = 3') , title('k = 4').**

Exercice N°3 (07pts)

1- Définir une matrice $\mathbf{a} = \begin{pmatrix} 1 & 2 & 3 & 5 & 9 \\ 4 & 5 & 6 & 8 & 7 \\ 7 & 8 & 9 & 6 & 4 \\ 9 & 3 & 1 & 0 & 6 \\ 5 & 6 & 7 & 8 & 1 \end{pmatrix}$

Ecrire les commandes matlab permettant de :
1. Calculer la matrice transposée de **a** (donnez le résultat d'application)
2. Extraire les éléments de la diagonale de **a.** (donnez le résultat d'application)
3. Supprimer la première colonne de **a** (donnez le résultat d'application)
4. Supprimer la première ligne de **a**(donnez le résultat d'application)
5. Extraire la sous-matrice obtenue par suppression de la seconde ligne et de la seconde colonne de **a.**

2- b- On veux construire la matrice 4x4 en utilisant la boucle for –end , tel que $A(i, k)=i^2+k^2$.

Bon courage

c) Donnez les significations et les résultats de calculs des ordres suivants. **A(2,6)= 10** , **A(: , 3)= 12**

Exercice N°2 (05pts)

Ecrire le programme Matlab qui permet de créer les tracés des quatre fonctions **sin(k pi x)** pour **x** entre [0, 401] le pas est 1 et k = 1, 2, 3, 4 dans une figure en utilisant les ordres **grid on ,subplot** et les titres **title('k = 1'), title('k = 2') , title('k = 3') , title('k = 4').**

Exercice N°3 (07pts)

1- Définir une matrice

$$\mathbf{a} = \begin{pmatrix} 1 & 2 & 3 & 5 & 9 \\ 4 & 5 & 6 & 8 & 7 \\ 7 & 8 & 9 & 6 & 4 \\ 9 & 3 & 1 & 0 & 6 \\ 5 & 6 & 7 & 8 & 1 \end{pmatrix}$$

Ecrire les commandes matlab permettant de :

1. Calculer la matrice transposée de **a** (donnez le résultat d'application)
2. Extraire les éléments de la diagonale de **a.** (donnez le résultat d'application)
3. Supprimer la première colonne de **a** (donnez le résultat d'application)
4. Supprimer la première ligne de **a**(donnez le résultat d'application)
5. Extraire la sous-matrice obtenue par suppression de la seconde ligne et de la seconde colonne de **a.**

2- b- On veux construire la matrice 4x4 en utilisant la boucle for –end , tel que $A(i, k)=i^2+k^2$.

Bon courage

Correction du contrôle 2016-2017 Inf pour la chimie

Exercice N°1(07pts) : Les instructions et les calculs matriciel a l'aide de Matlab.

a) signification des instructions suivantes.

polyval(p,m) : La commande polyval permet d'évaluer le polynôme p (la fonction polynômiale) en en un point donné m.

mod(a,b) : Ce qui donne le reste de la division de **a** sur **b.**

sign(x) : Donner un signal qui donne le nombre 1 si le nombre est supérieur à partir de zéro, donnant -1 Si le nombre est très inférieur à zéro.

abs(z) : C'est le module du nombre complexe

horner(f): Simplifie la fonction de sa forme dans Matlab en forme de produit d'une puissance croissante.

compose(f,g) :C'est l'ordre qui composes fonctions uns avec les autres.

hold on :Utilisation pour représenter deux courbes dans une forme d'exemple.

-La différence entre (» **legnth(A)** et » **size(A)**)

legnth(A) : C'est le nombre de lignes d'une matrice .

size(A) : C'est le nombre de lignes et de colonnes d'une matrice

b) Soit les polynômes suivants :

$$a(x) = x^4 - 2x^3 + 11 \quad , \quad b(x) = x^2 - 2x + 15.$$

Représentation des vecteurs des polynômes (sur Matlab)

```
a = [1 -2 0 6 11];
b = [1 -10 15];
```

Use polyder to calculate

$$q(x) = \frac{d}{dx}\left[a(x)b(x)\right].$$

```
q = polyder(a,b)
```

```
q =

     6   -60   140   -90    22  -110
```

The result is

$$q(x) = 6x^5 - 60x^4 + 140x^3 - 90x^2 + 22x - 110.$$

2- Soit la matrice suivante. A=

a) Nommez et écrivez la matrice **D :**

D =A([5 8 13 20 26 32 ; 4 10 17 23 31 36 ; 36 11 18 22 6 19 ; 30 7 10 27 16 29])

```
>> A=[47,58,69, 80,1,12; 57,68,79,9,11,22;67,78,8,10,21,32;77,7,18,20,31,42;6,17,19,30,41,52;16,27,29,40,51,62]
A =

    47    58    69    80     1    12
    57    68    79     9    11    22
    67    78     8    10    21    32
    77     7    18    20    31    42
     6    17    19    30    41    52
    16    27    29    40    51    62

>> D =A([5 8 13 20 26 32 ; 4 10 17 23 31 36 ; 36 11 18 22 6 19 ; 30 7 10 27 16 29])
D =

     6    68    69     9    11    22
    77     7    19    30    12    62
    62    17    29    20    16    80
    51    58     7    21    18    41
```

b) Ajouter les six nombres suivants **8, 9 ,10 ,11 3 2** sur la **6^{éme}** ligne.(donnez la forme de la nouvelle matrice)

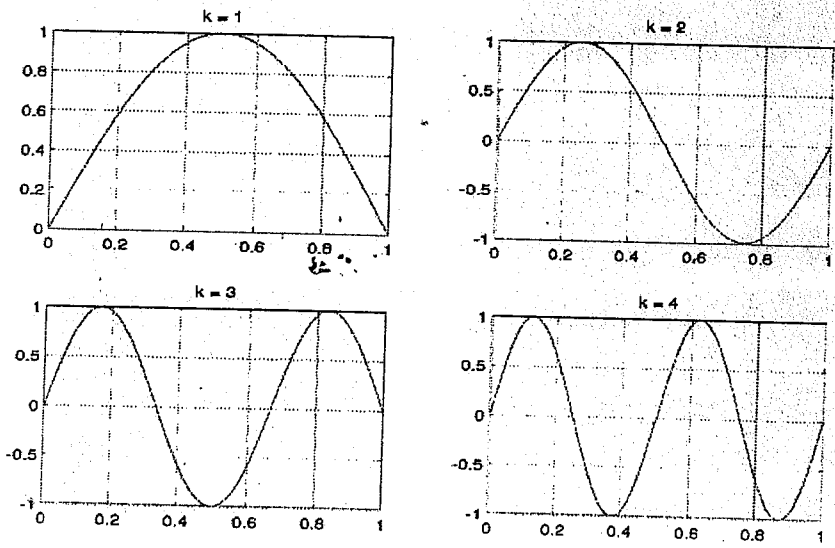
```
>> D(6,1:6)= [8, 9 ,10 ,11 3  2]

D =

     6    68    69     9    11    22
    77     7    19    30    12    62
    62    17    29    20    16    80
    51    58     7    21    18    41
     0     0     0     0     0     0
     8     9    10    11     3     2
```

les significations et les résultats de calculs des ordres suivants.

A(2,6)= 10 : Changer l'élément A(2,6) par le nombre 10.

A(: , 3)= 12 : remplacer tout les elements de la colonne 3par le nombre 12.

```
x = linspace(0, 1, 401);
>>  subplot(2,2,1)
>> plot(x, sin(1*pi*x))
>> grid on; title('k = 1')
>> subplot(2,2,2)
>>  plot(x, sin(2*pi*x))
>> grid on; title('k = 2')
>> subplot(2,2,3)
>> plot(x, sin(3*pi*x))
>> grid on; title('k = 3')
>> subplot(2,2,4)
>>  plot(x, sin(4*pi*x))
>> grid on; title('k = 4')
```



```
>> for (i= 1:4)
for (k = 1:4)
A(i,k)= i^2 +k^2;
end
end
>> disp(A)
     2     5    10    17
     5     8    13    20
    10    13    18    25
    17    20    25    32
```

Université El-oued
Faculté des sciences exacte
Département de chimie
1ère Master

2016/2017

Examen de chimie organique quantique

Question de cours (vrai/faux) :(06pts)

1. La premiere postulas de la mecanique quantique :Toute particule, ou plus généralement tout système quantique, est partiellement défini à l'instant **t** par une fonction complexe **ψ (r,t)** appelée fonction d'onde. Toutes les informations accessibles concernant le système à l'instant t se déduisent de la connaissance de ψ à cet instant.

2. la 4eme postulats de la mecanique quantique :Soit un système décrit par la fonction d'onde :
   $\psi(\mathbf{r},t) = \sum_n c_n(t)\,\varphi_n(\mathbf{r})$
   La probabilité que le résultat de la mesure de la grandeur physique A soit, à l'instant **t**, $\mathbf{a_p}$ est $\mathbf{|c_p(t)|^2}$.

3. L'équation de Schrödinger en unite atomique est :
   $$-\frac{\hbar^2}{2m}\Delta\Psi(x,y,z)-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\sqrt{x^2+y^2+z^2}}\Psi(x,y,z)=E\Psi(x,y,z)$$

4. Approximation de Born-openheimer: l'hypothèse simplificatrice qui consiste à considérer que les noyaux, beaucoup plus lourds que les électrons, peuvent être supposés immobiles pendant que les électrons se déplacent autour d'eux. Donc l'energie cenitique des noyons est nul .

5. L'operateur hamiltonien s'écrit, dans 1'hypothèse ou la masse du noyau est supposée infiniment grande devant celle de 1'électron:
   $$H=\sum_i\left[-\frac{\hbar^2}{2m_e}\Delta_i-\frac{Ze^2}{4\pi\epsilon_o r_i}\right]+\sum_{i<j}\frac{e^2}{4\pi\epsilon_o r_{ij}}$$

6. L'operateur hamiltonien s'écrit, dans 1'hypothèse ou la masse du noyau est supposée infiniment grande devant celle de 1'électron :
   $$H=\sum_i\left(-\frac{1}{2}\Delta_i-\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}}$$

EXERCICE :(14pts)

Etudie la molecule butadiene par la methode de huckel.

Module : Chimie Organique générale

Question de cours (4 pts)

1 → F (0,5) 4 → V (0,5)

2 → V (0,5) 5 → V (0,5)

3 → F (0,5) 6 → V (0,5)

Exercice (14 pts)

La molécule butadiène

$C = C - C = C$ (0,5) $\quad \det = |H_{ij} - E S_{ij}| = 0$

$$\det \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$ (0,5)

$H_{ii} = \alpha$ (0,5) $\quad H_{ij} = \beta$ (0,5)

$S_{ii} = 1$ (0,5) $\quad S_{ij} = 0$

on pose $x = \frac{\alpha - E}{\beta}$ (0,25)

$$\Rightarrow \det = \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$ (0,5)

$\begin{cases} x_1 = 1,618 \text{ (0,5)} \\ x_2 = -1,618 \text{ (0,5)} \end{cases} \quad \begin{cases} x_3 = 0,618 \text{ (0,5)} \\ x_4 = -0,618 \text{ (0,5)} \end{cases}$

Les configurations

$x_1 = -2\cos\left(\frac{\pi}{5}\right) = -1,618$ (0,5)

$x_2 = -2\cos\left(\frac{2\pi}{5}\right) = -0,618$ (0,5)

Les énergies

$E_1 = \alpha + 1,618\beta$ (0,5) E_4 —

$E_2 = \alpha + 0,618\beta$ (0,5) E_3 —

$E_3 = \alpha - 0,618\beta$ (0,5) E_2 —

$E_4 = \alpha - 1,618\beta$ (0,5) E_1 —

Les coefficients :

pour N_1 : $C_1 = C_4 = 0,37$, $C_2 = C_3 = 0,60$ (0,25 x 4)

pour N_2 : $C_1 = C_4 = 0,60$ $C_2 = C_3 = 0,37$ (0,25 x 4)

pour N_3 : $C_1 = C_4 = 0,60$ $C_2 = C_3 = 0,37$ (0,25 x 4)

pour N_4 : $C_1 = C_4 = 0,37$ $C_2 = C_3 = 0,60$ (0,25 x 4)

Les Orbitales Moléculaires

$\Psi_1 = 0,37\Phi_1 + 0,60\Phi_2 + 0,60\Phi_3 + 0,37\Phi_4$ (0,5)

$\Psi_2 = 0,60\Phi_1 + 0,37\Phi_2 + 0,37\Phi_3 + 0,60\Phi_4$ (0,5)

$\Psi_3 = 0,60\Phi_1 - 0,37\Phi_2 + 0,37\Phi_3 - 0,60\Phi_4$ (0,5)

$\Psi_4 = 0,37\Phi_1 - 0,60\Phi_2 + 0,60\Phi_3 - 0,37\Phi_4$ (0,5)