

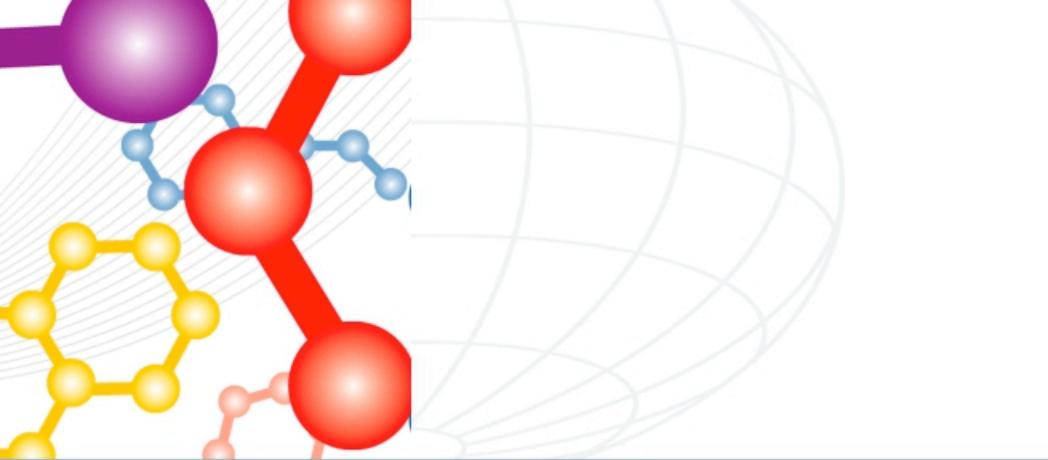


# Chimie des Biomolécules

PACES UE1

Pr. Nicolas Willand

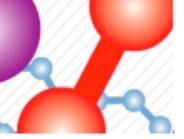




## Chapitre 1: les Lipides

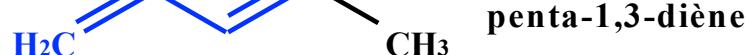
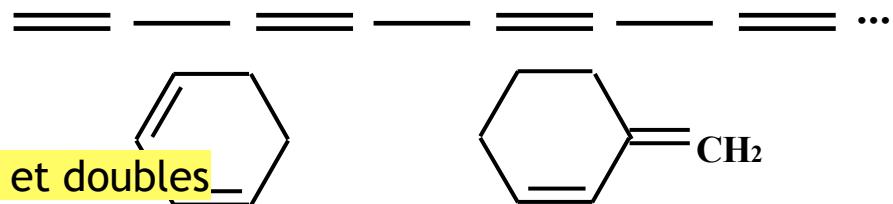
### Partie 1.4 : les polyènes conjugués





# Partie 1.4.0 : Définition de la conjugaison

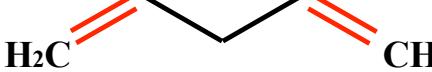
## Définition, Nomenclature



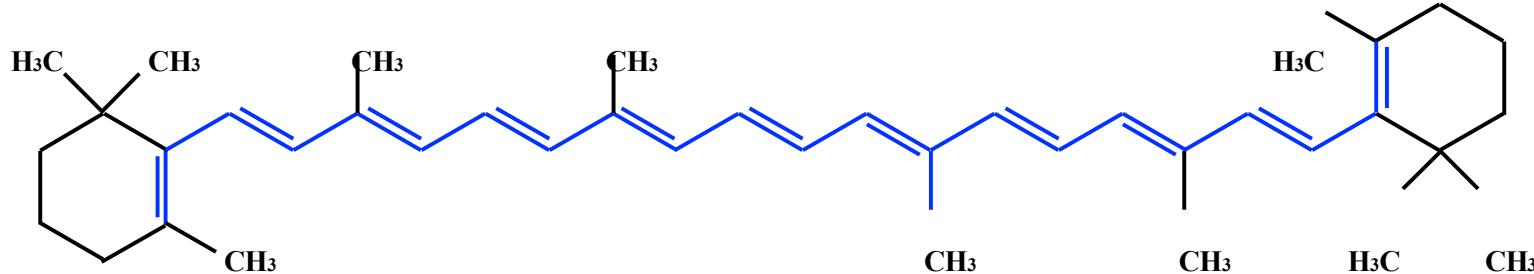
diènes conjugués

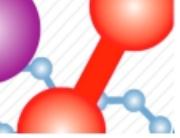


cumulènes  
diènes isolés



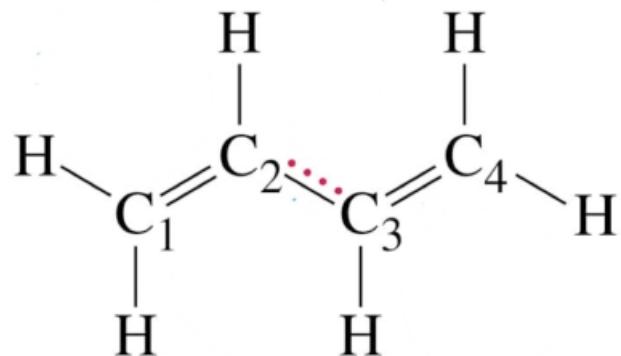
diènes, non conjugués



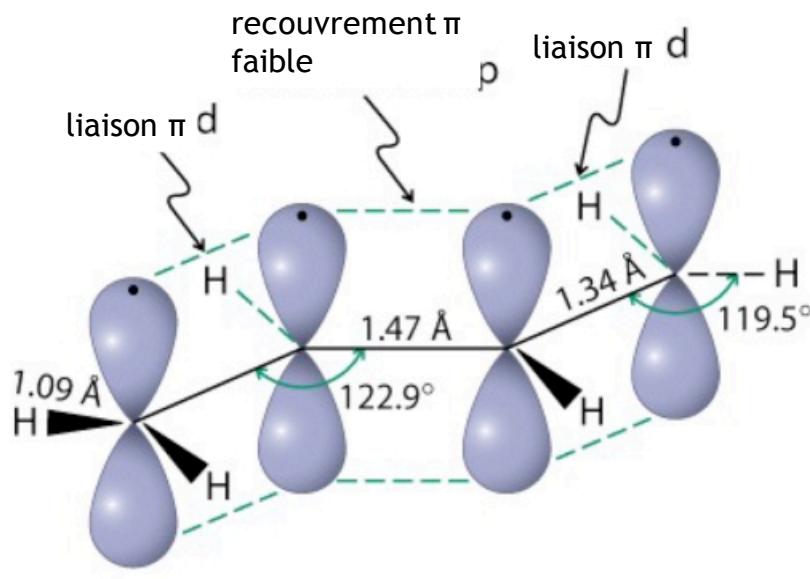


# Partie 1.4.0 : structure des diènes conjugués

## le butadiène



$\text{sp}^2 \quad \text{sp}^2 \quad \text{sp}^2 \quad \text{sp}^2$

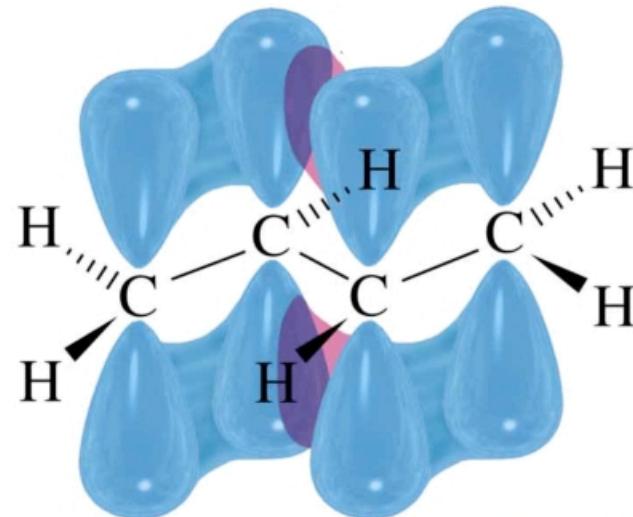


$1,34 \quad 1,47 \quad 1,34 < 1,54 \text{ \AA}$

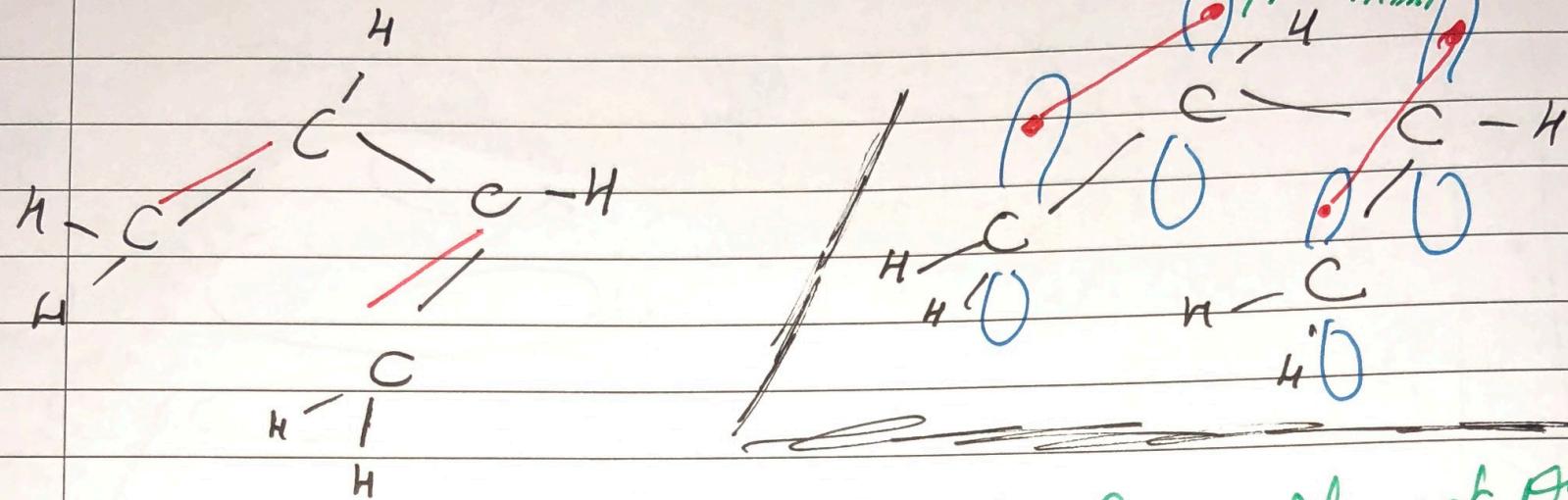
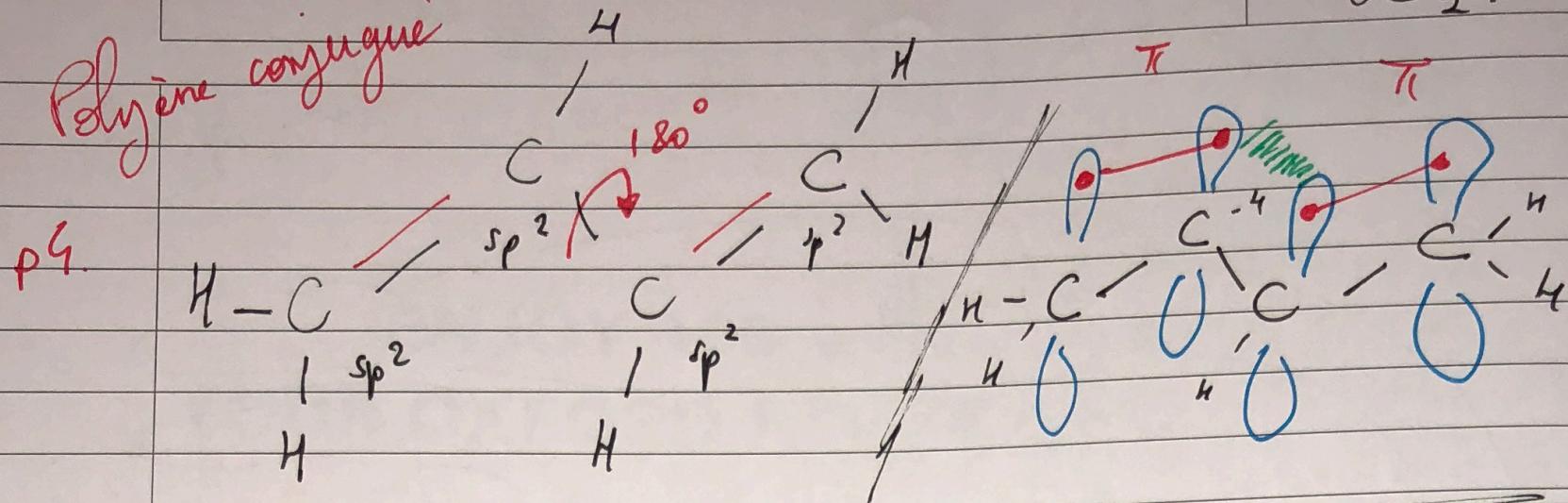
$\text{sp}^3 \quad \text{sp}^3 \quad \text{sp}^2 \quad \text{sp}^2$



$1,54 \quad 1,34$

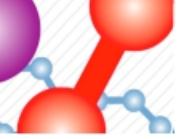


Polyène conjugué

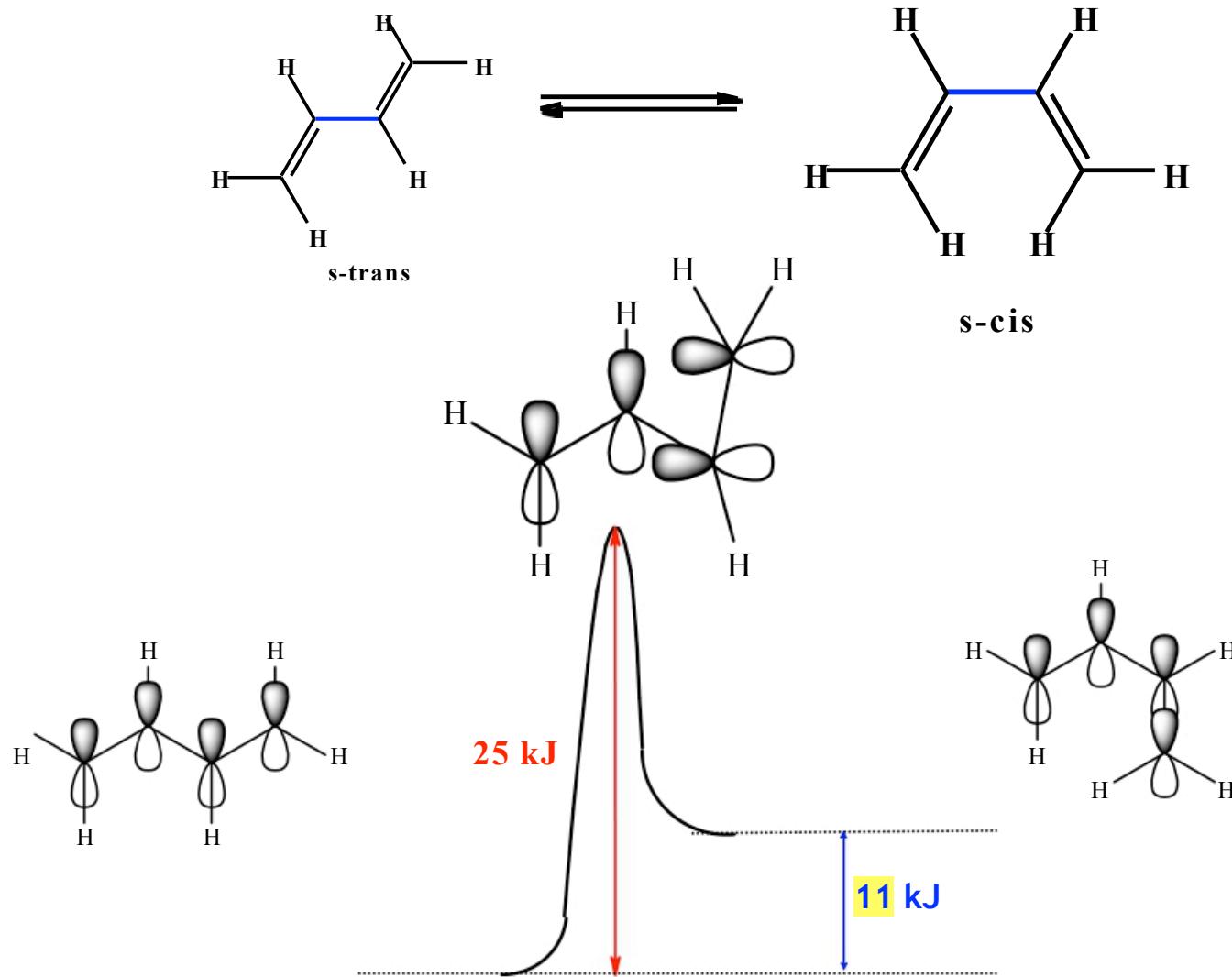


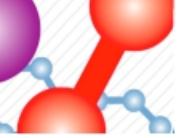
III  $\Rightarrow$  interac<sup>θ</sup>: amide rotat<sup>θ</sup>.

# Partie 1.4.0 : structure des diènes conjugués



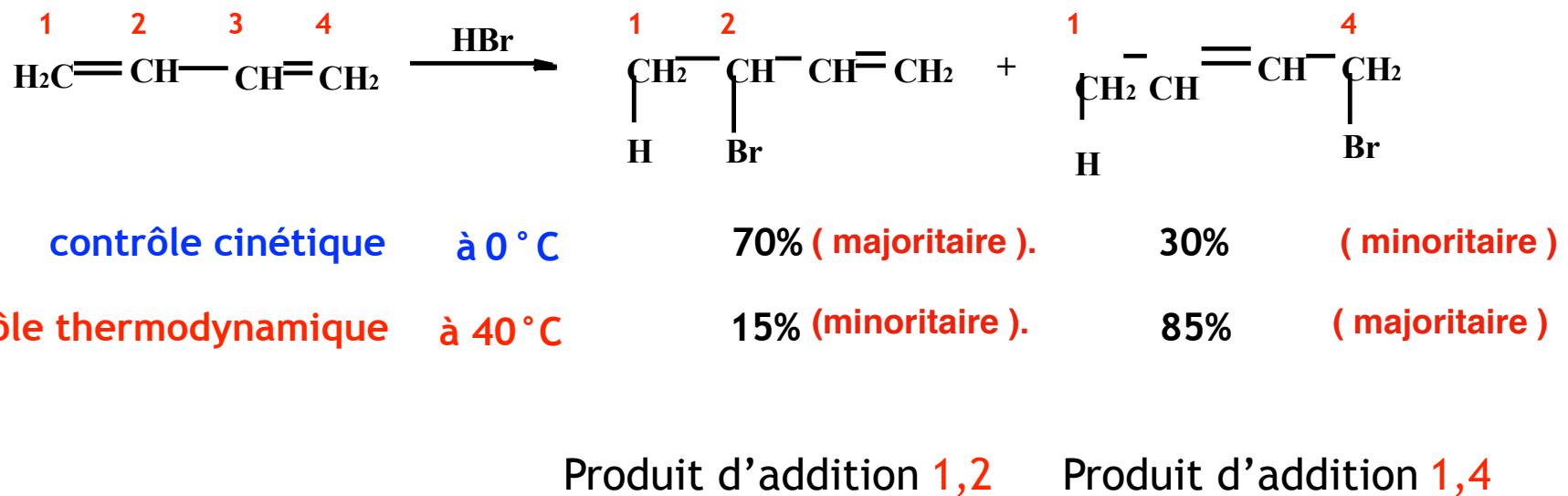
## conformations limites du butadiène

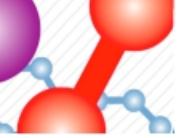




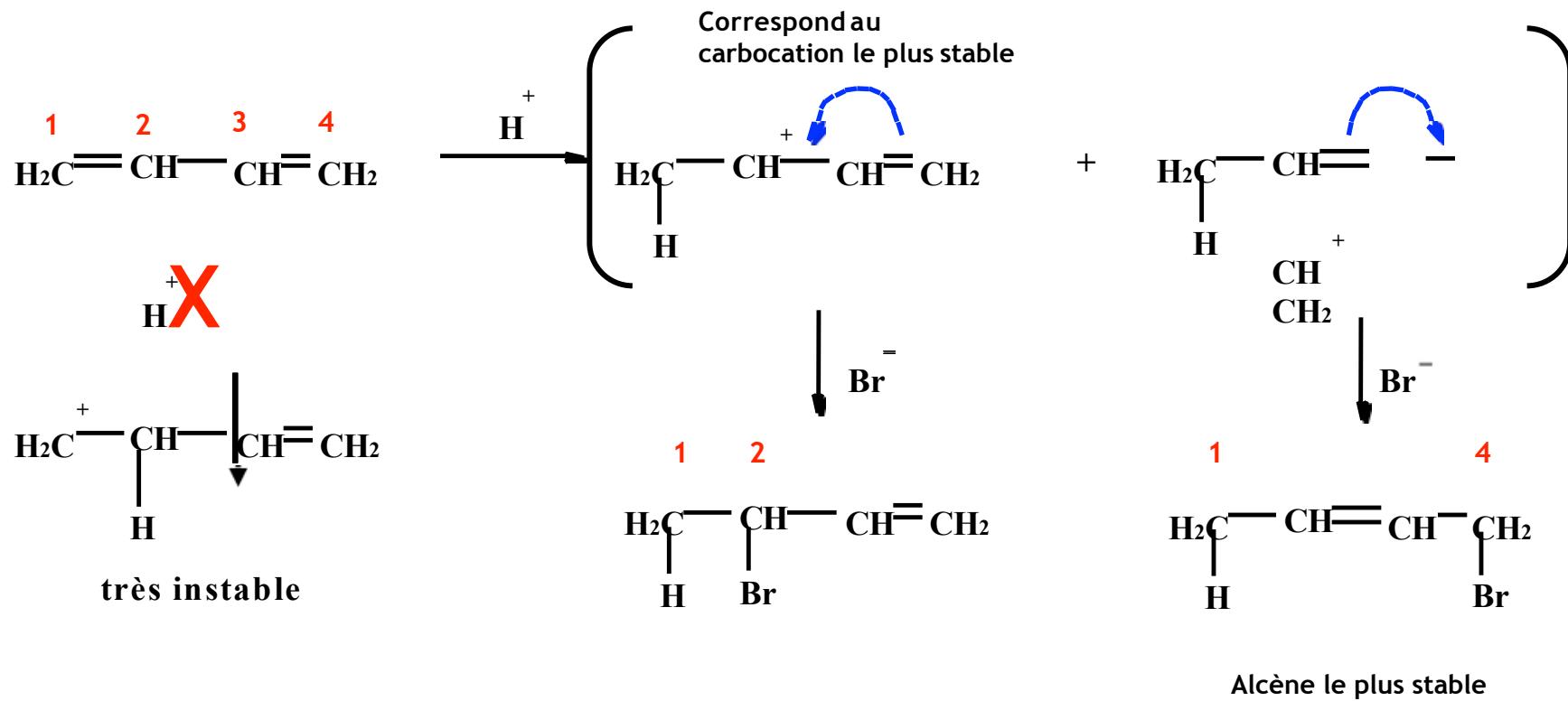
## Partie 1.4.0 : Propriétés chimiques des diènes conjugués

### Addition électrophile sur le butadiène





## Partie 1.4.0 : Propriétés chimiques des diènes conjugués



p  
r

le produit cinétique correspond au carbocation le plus stable

le produit thermodynamique correspond à l'alcène le plus substitué



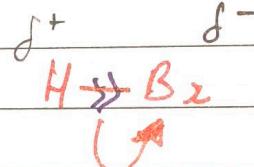
p.

C<sub>6</sub>H<sub>6</sub>

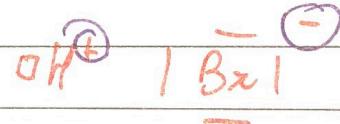
-Na



$\sigma$ -trans-5



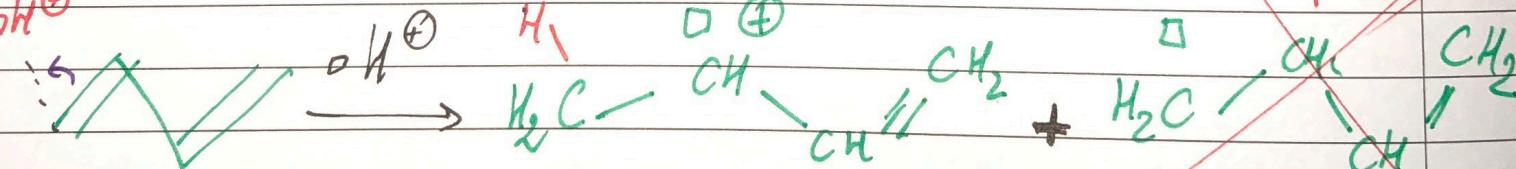
Rupture  
heterolytig  $2e^-$



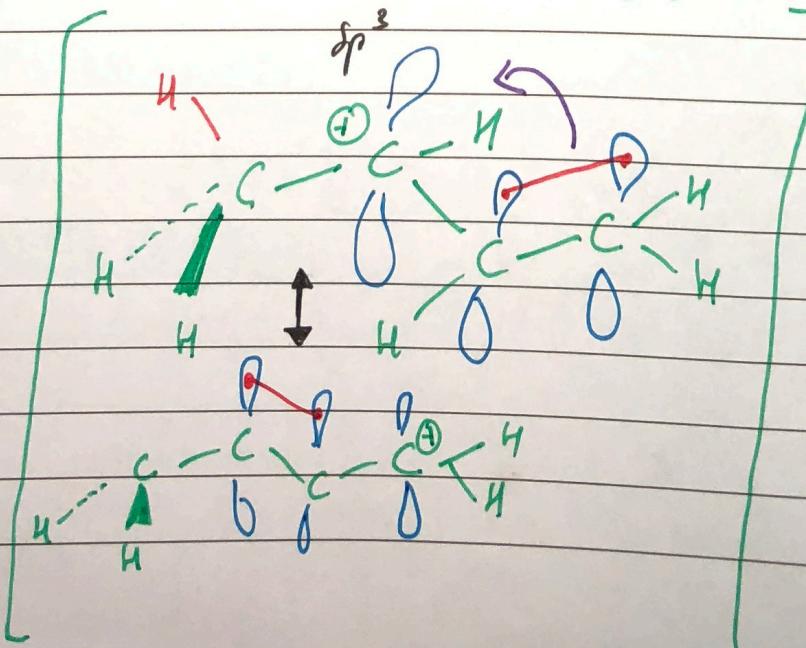
$\text{C}^{\text{II}} \nu$

$\text{C}^{\text{I}} \nu$

$\text{OH}^{\oplus}$



$\ominus$  stable



11

OP

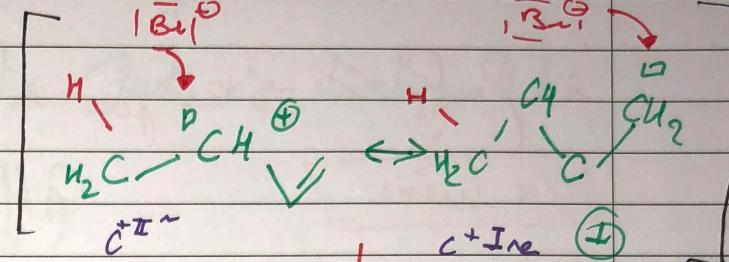
$\text{C}^{II^-}$  en 1<sup>er</sup> flu de ...

$\square \text{H}^+$



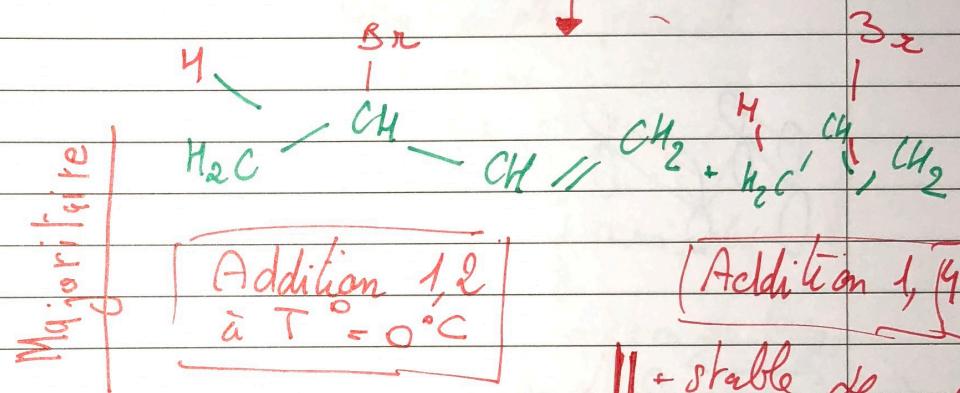
$\text{H}^+$

### NÉOISOMÉRIE

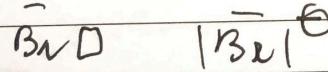
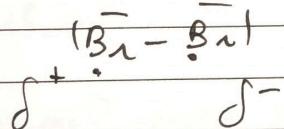


$\text{A} \text{B}^{II^-}$   
m favorise Prochain am<sup>tg</sup>.  
pas p stim' de C+ stable

$\text{Br}^0 \ominus$



$\text{C}^{I\text{ne}} \rightarrow \text{Add. O} + \text{stalle}$

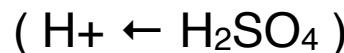


// + stable p  
doubt p sur l°

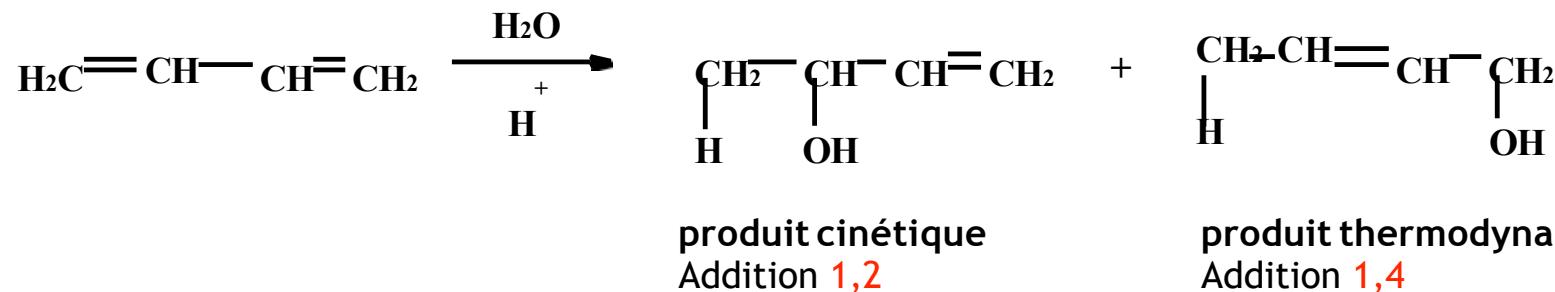


## Partie 1.4.0 : Propriétés chimiques des diènes conjugués

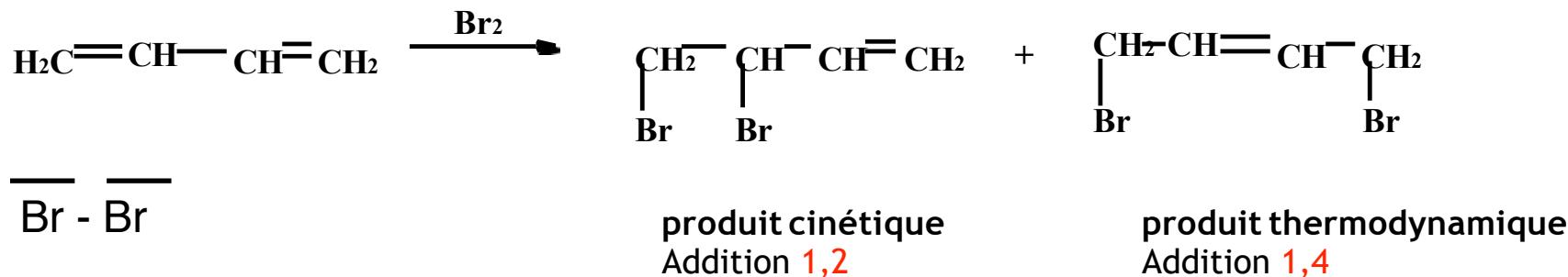
### autre réaction d'addition:



#### hydratation:



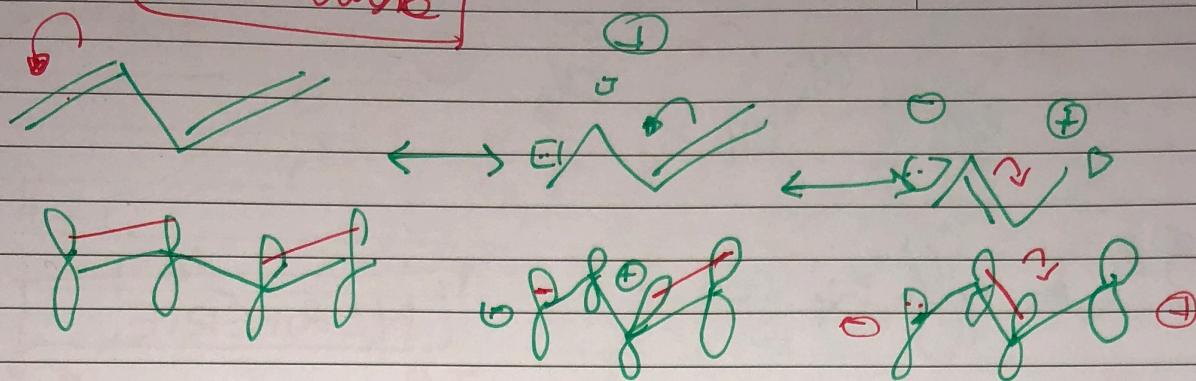
#### Halogénéation:



Polarisable  
OA volumineuses

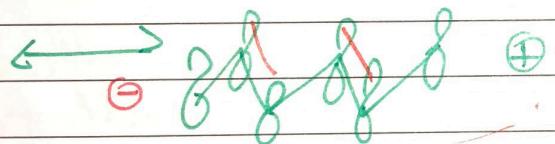
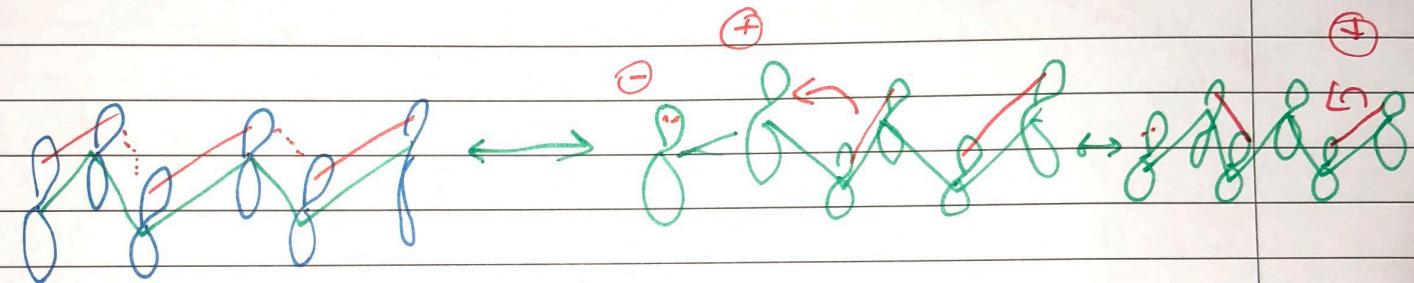
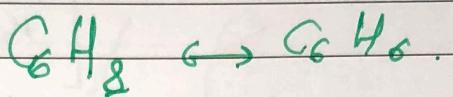


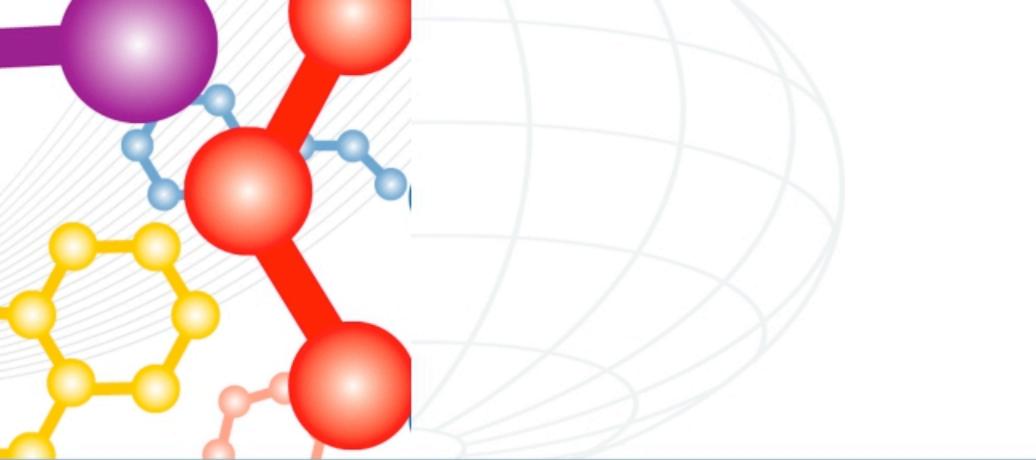
p 8



si  $\delta\delta \leftrightarrow e^-$  pas un à 0 keV

flexation





## Chapitre 1: les Lipides

### Partie 1.4 : les arènes





## Partie 1.4 : Les Arènes

### Partie 1.4.1: Généralités

#### Le benzène

- Isolé en 1825 par Faraday dans le liquide résiduel du fond des bouteilles d'éclairage. Produit issu de la pyrolyse d'huile de baleine et il détermine un rapport C:H de 1:1. Il le nomme « bi-carburet of hydrogen »





# Partie 1.4 : Les Arènes

## Partie 1.4.1: Généralités

### • Le benzène

- Isolé en 1825 par Faraday dans le liquide résiduel du fond des bouteilles d'éclairage. Produit issu de la pyrolyse d'huile de baleine et il détermine un rapport C:H de 1:1. Il le nomme « bi-carburet of hydrogen »
- « Synthétisé » en 1834 par Eilhard Mitscherlich par chauffage d'acide benzoïque avec de l'oxyde de Calcium. Il mesure également sa masse moléculaire et montre qu'elle correspond à  $C_6H_6$ . Il le nomme « benzène »
- C'est à l'odeur parfois agréable de ces dérivés que l'on doit le terme:

**“hydrocarbures aromatiques”**

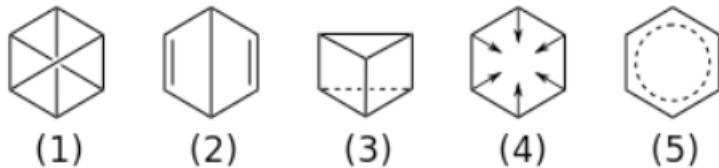


# Partie 1.4 : Les Arènes

## Partie 1.4.1: Généralités

- Le benzène

$C_6H_6$  ?

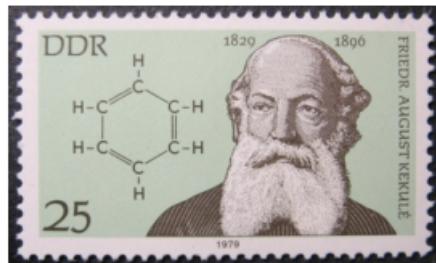


Kathleen Lonsdale

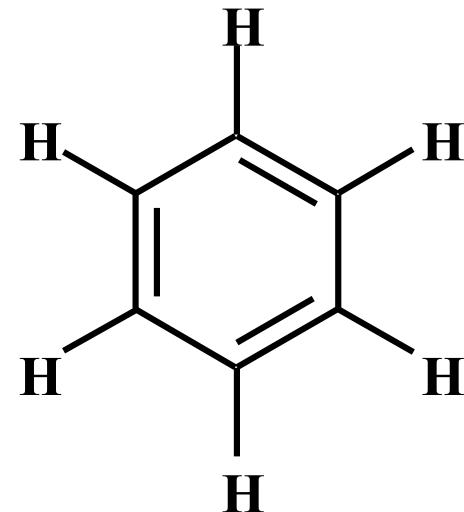


Structures du benzène historiquement proposées par

- (1) Claus (1867)
- (2) Dewar (1867)
- (3) Ladenburg (1869)
- (4) Armstrong (1887)
- (5) Thiele (1899)



Structure cyclique avec une alternance de simples et de doubles liaisons



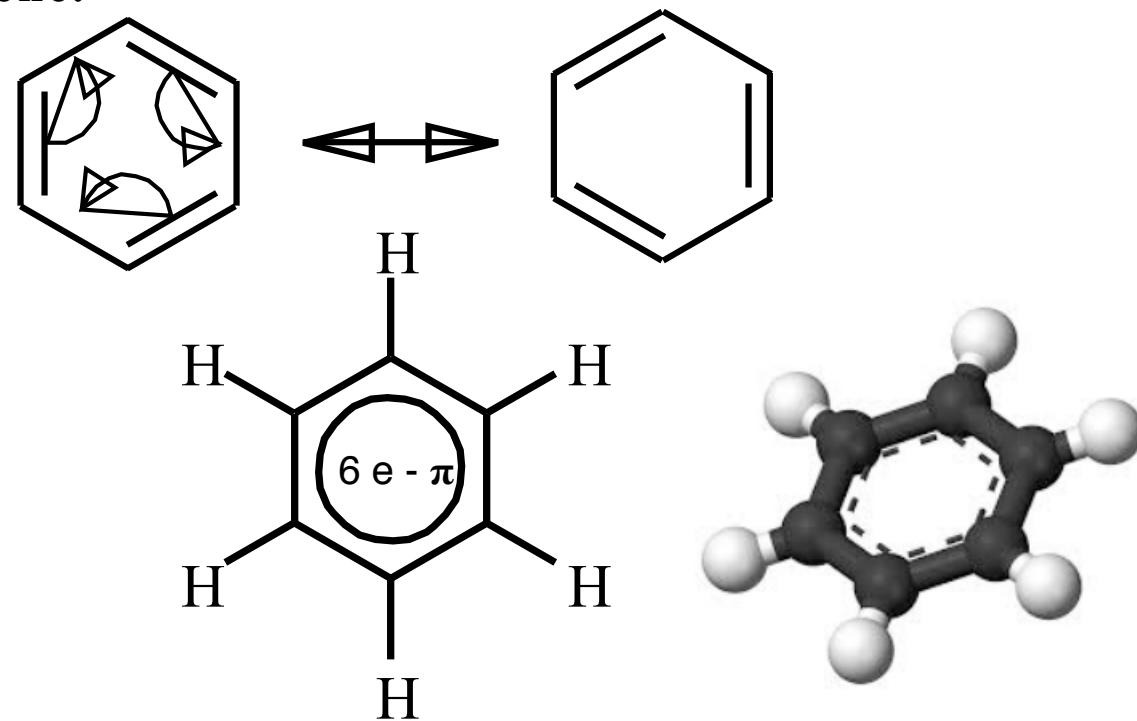


## Partie 1.4 : Les Arènes

### Partie 1.4.1: Généralités

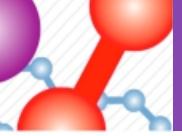
- **Le benzène**

Il est possible d'écrire deux structures en résonance/ mésomères de la molécule de benzène.



Les 6 électrons délocalisés peuvent être représentés par un cercle





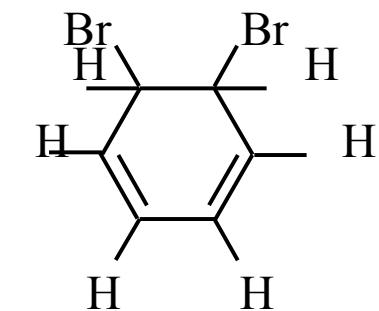
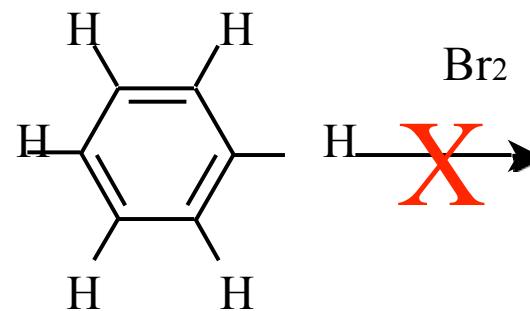
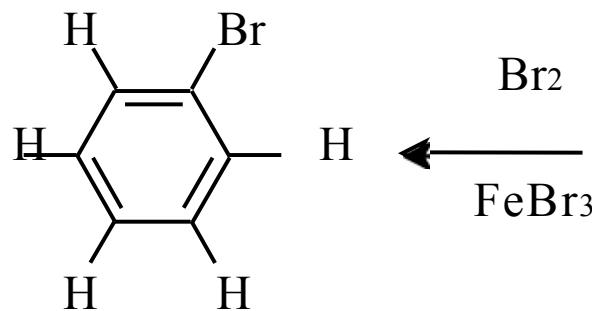
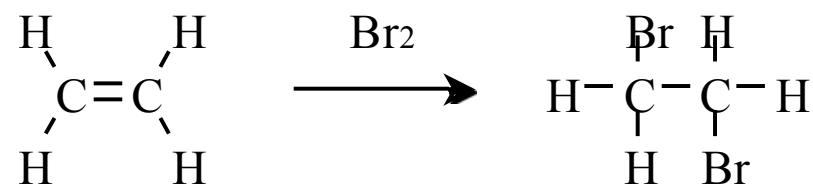
# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

- Le benzène

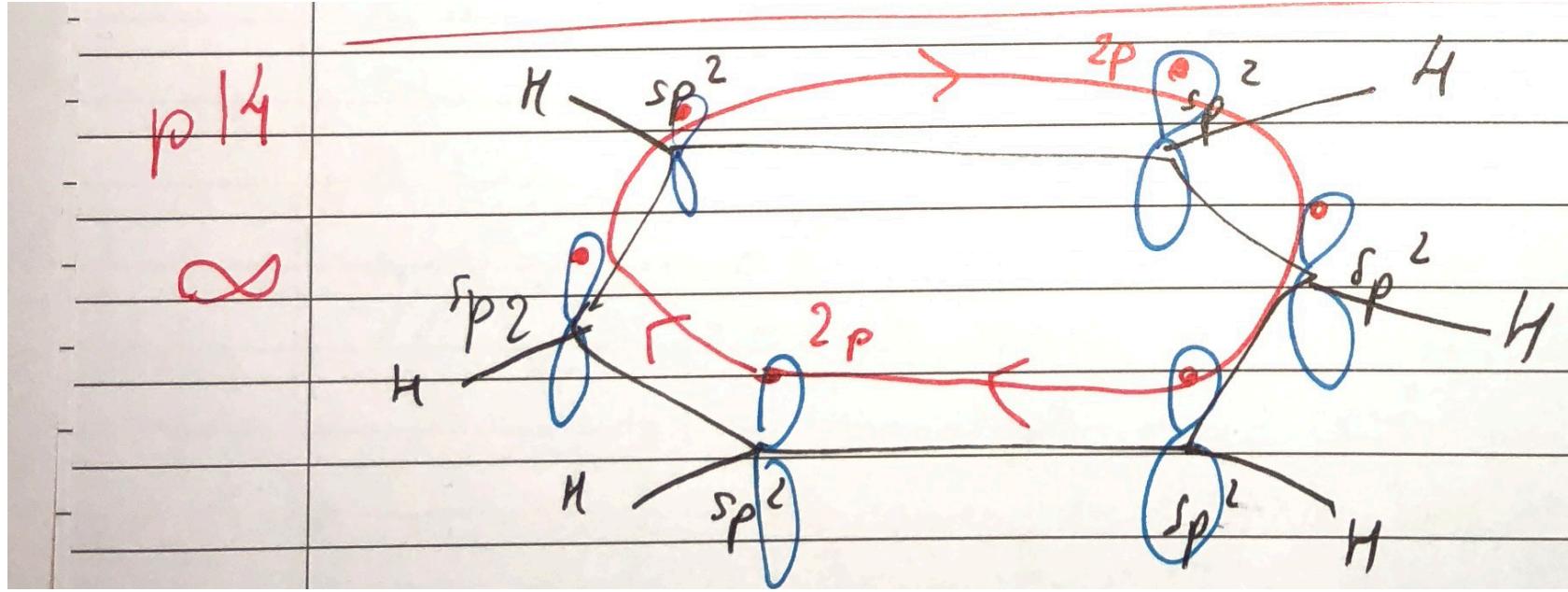
### REACTIVITE

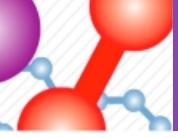
### Addition



### Substitution







## Partie 1.4 : Les Arènes

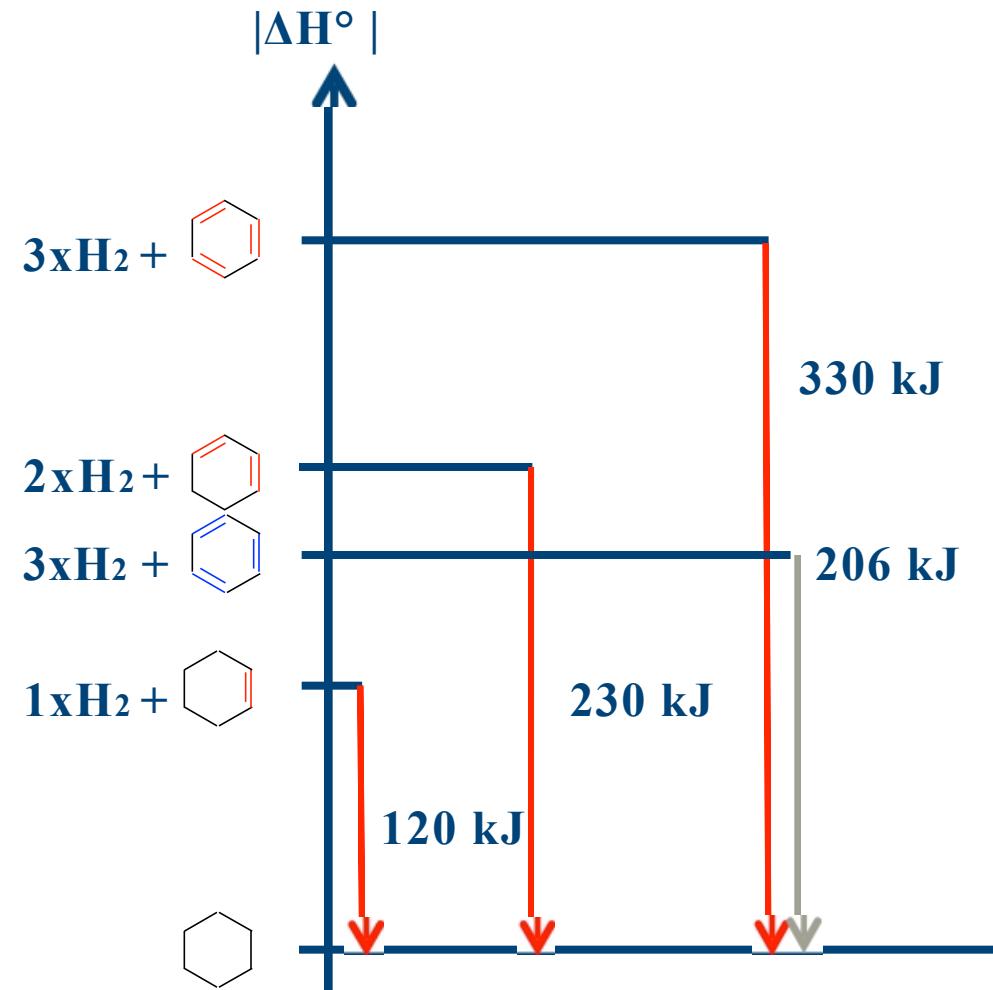
### Partie 1.4.2: La réactivité des hydrocarbures aromatiques

Cyclohexa-1,3,5-triène

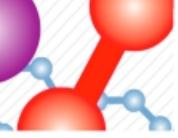
Cyclohexa-1,3-diène  
benzène

Cyclohexène

Cyclohexane



Énergie de résonance (stabilisation) = 124 kJ



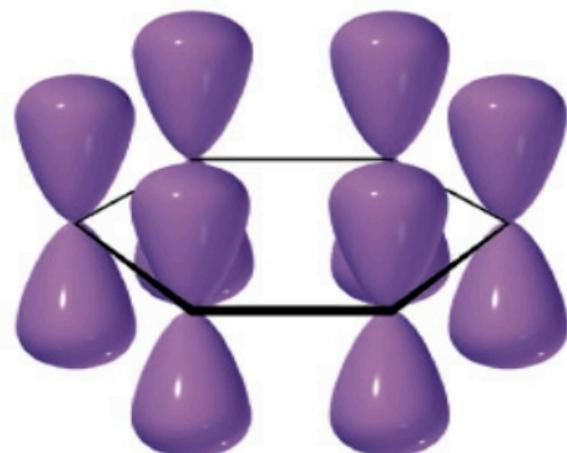
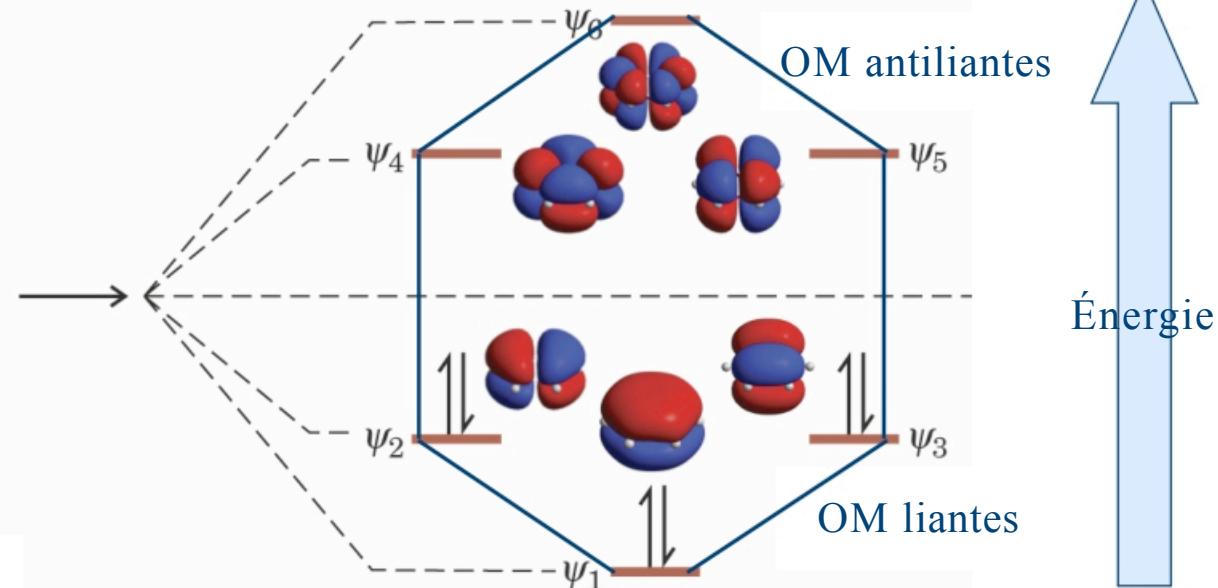
## Partie 1.4 : Les Arènes

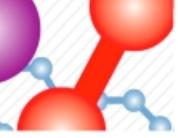
### Partie 1.4.2: La réactivité des hydrocarbures aromatiques

#### Structure électronique : Orbitales Moléculaires

1 1 1 1 1 1

Six orbitales 2p  
Contiennent six  
électrons



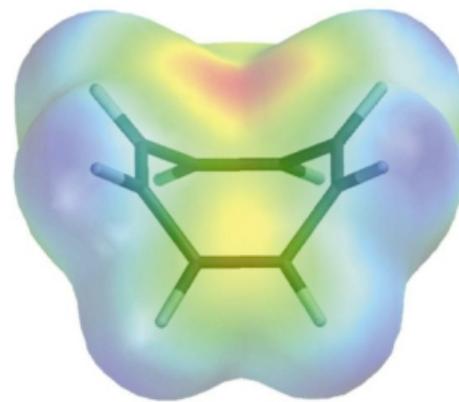
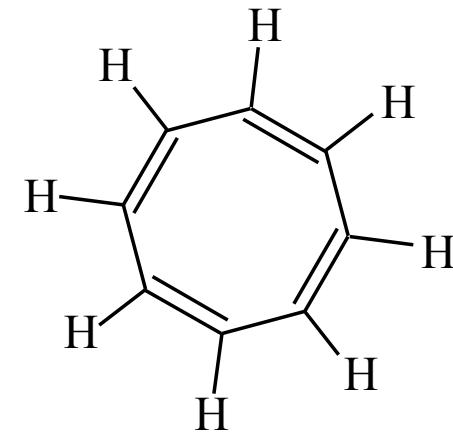


# Partie 1.4 : Les Arènes

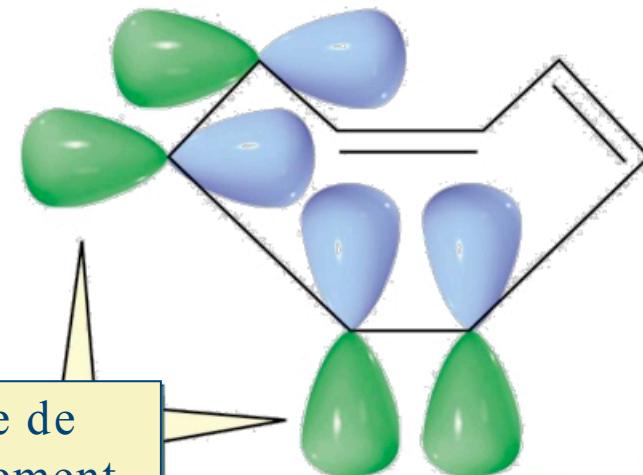
## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

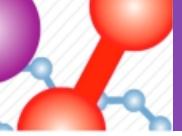
### Le cyclooctatétraène

- Homologue supérieur du benzène
- Cycle contenant 4 liaisons  $\pi$
- Molécule très instable sous l'action de la chaleur, comportement similaire à celui d'un alcène
- Molécule non plane
- Le cyclooctatétraène ne présente donc pas de caractère aromatique



Absence de recouvrement





## Partie 1.4 : Les Arènes

### Partie 1.4.2: La réactivité des hydrocarbures aromatiques

#### Règle de Hückel

● Aromatique:

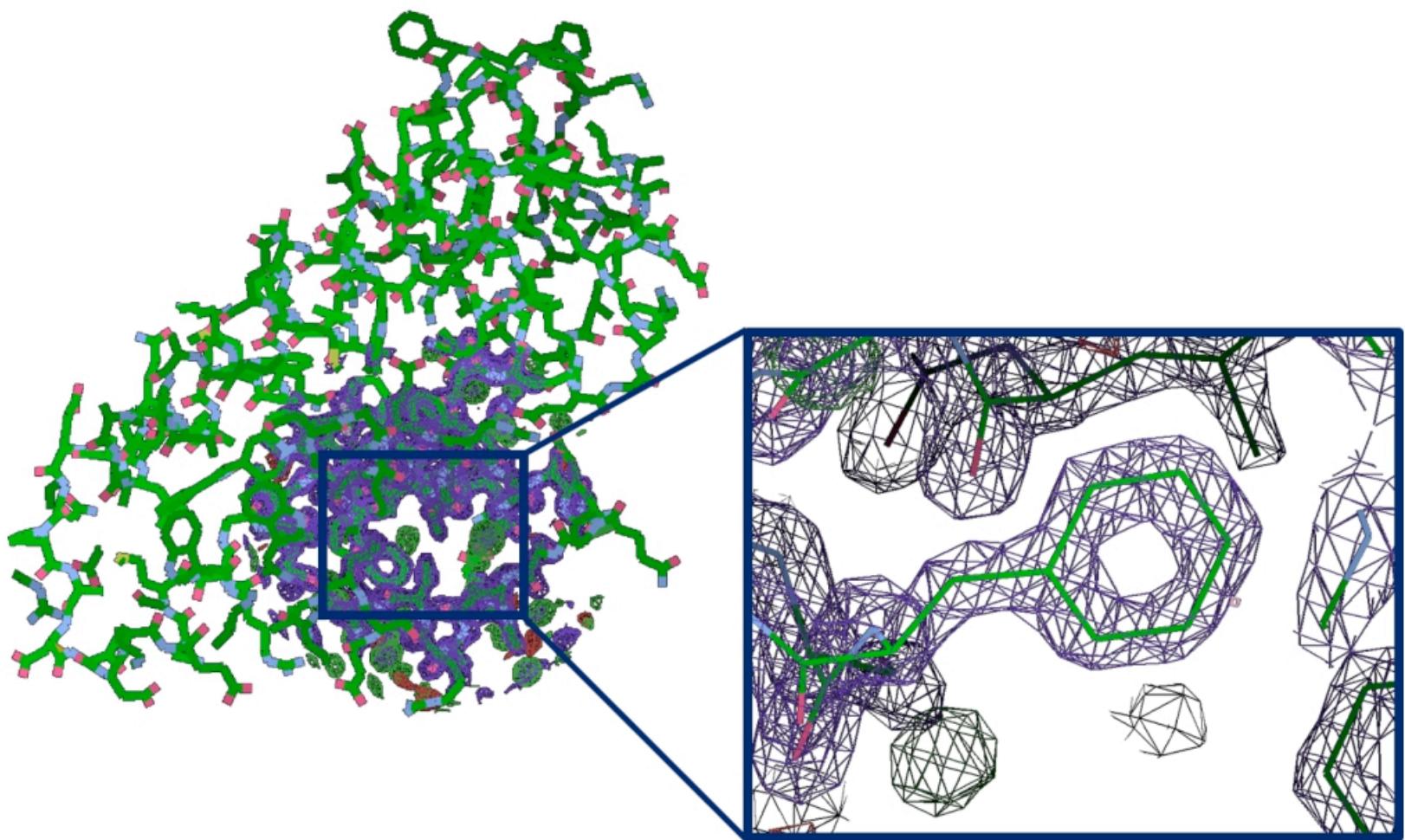
- polyènes conjugués cycliques plans
- orbitale p au niveau de chaque atome du cycle
- Possédant  $4n+2$  électrons  $\pi$  ( $n = 0, 1, 2, 3 \dots$ )

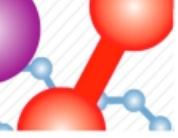
● Non aromatique:

- non coplanaires: le **recouvrement cyclique est interrompu** pour conférer à la molécule des propriétés comparables aux alcènes
- Critères: n<sup>bre</sup> électrons  $\pi \neq 4n+2$  et/ou non plan



# Exemple d'une phénylalanine

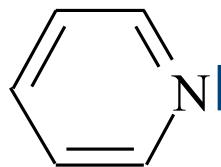
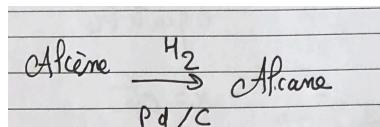




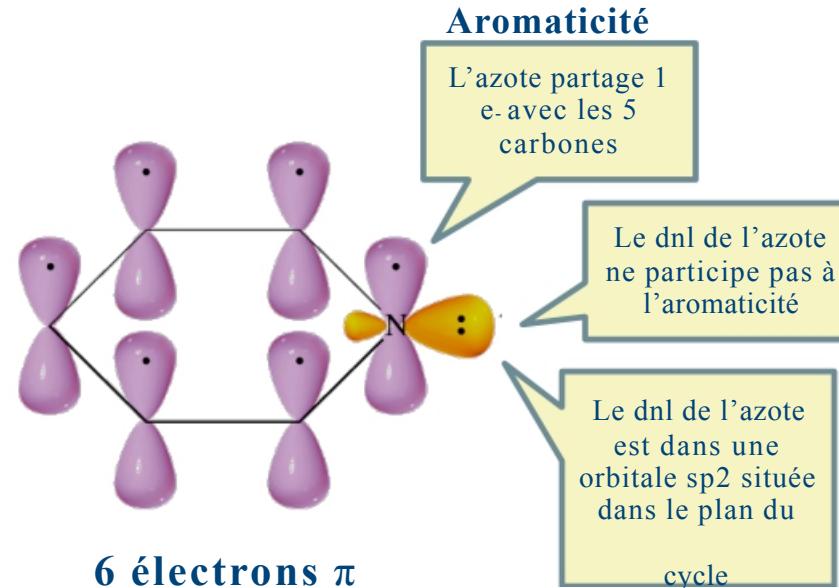
# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

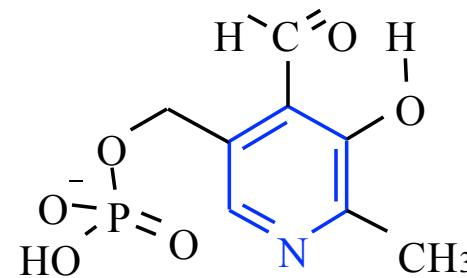
### • Hétérocycles aromatiques à 6 sommets



**Pyridine**



### • Exemple: le phosphate de pyridoxal



**pyridine**



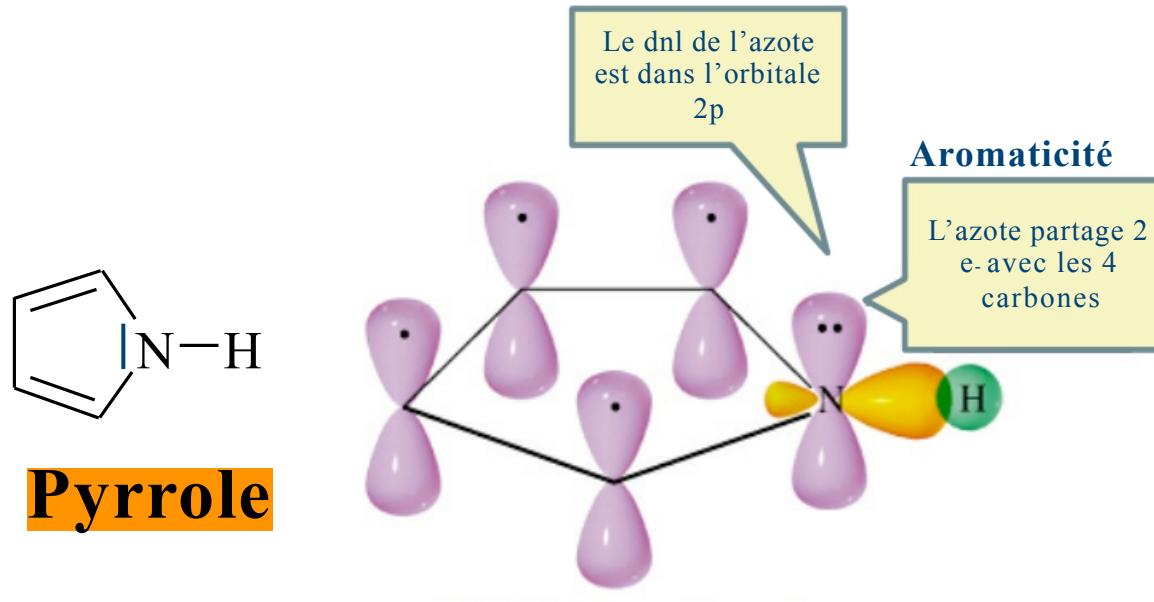




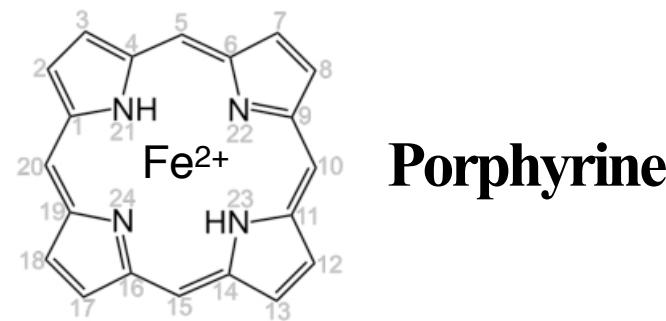
# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

### • Hétérocycles aromatiques à 5 sommets

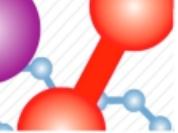


Exemple:

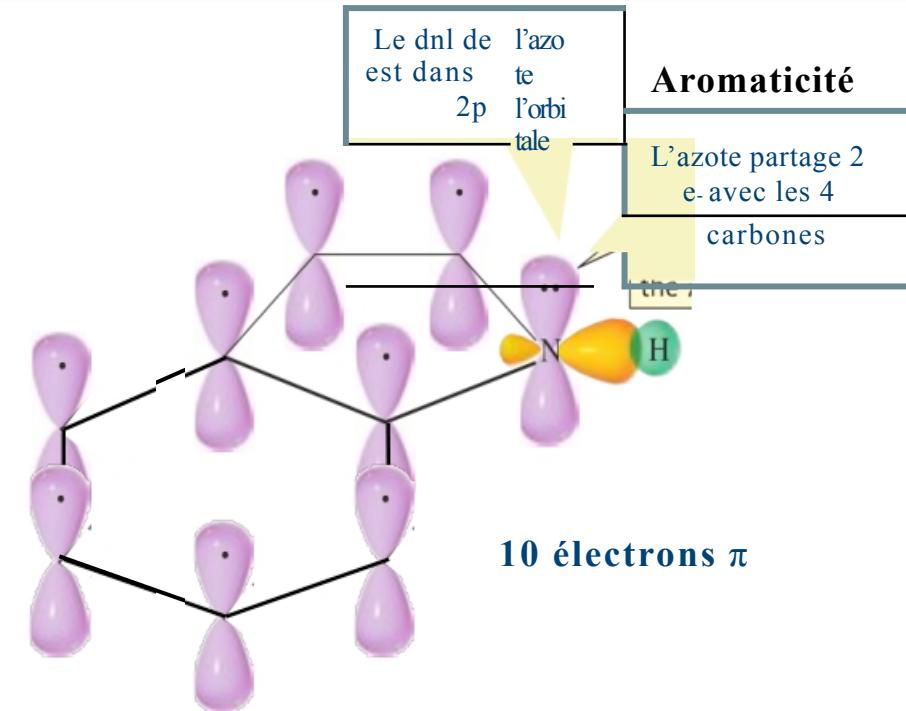
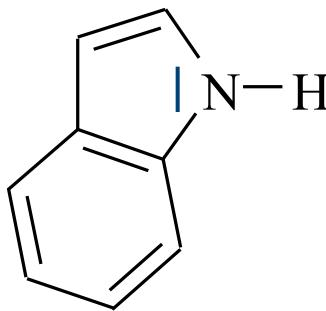


Porphyrine

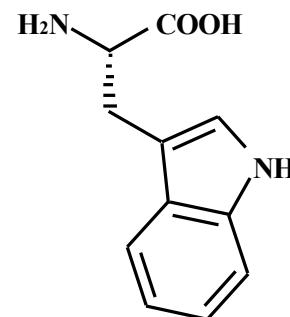
# Partie 1.4 : Les Arènes



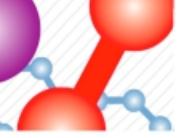
## Partie 1.4.2: La réactivité des hydrocarbures aromatiques



Exemple: Le tryptophane



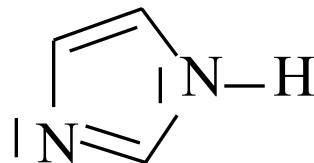
Tryptophane  
Trp  
W



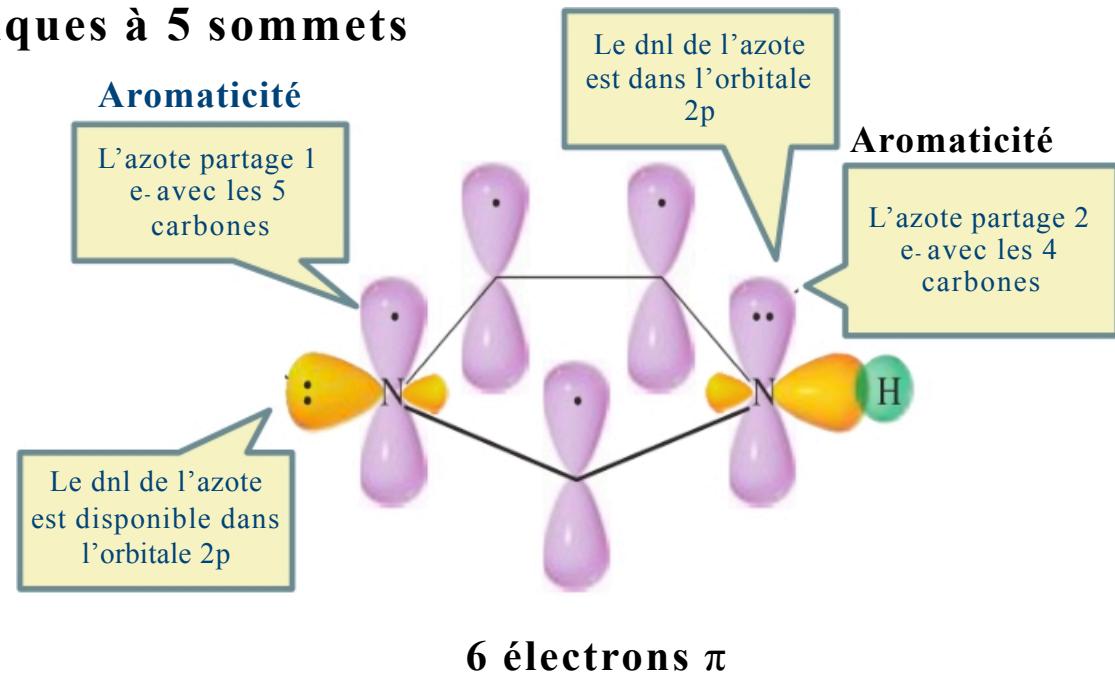
# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

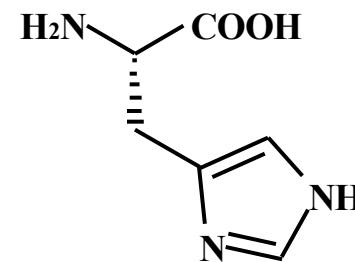
### Hétérocycles aromatiques à 5 sommets



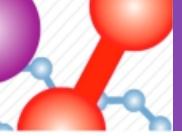
**Imidazole**



### Exemple: l'histidine



**Histidine**  
His  
H



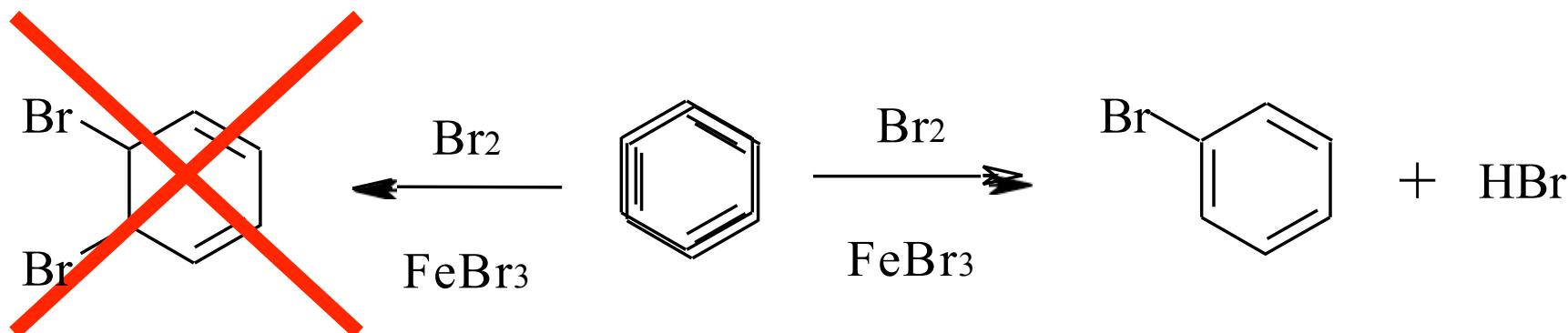
## Partie 1.4 : Les Arènes

### Partie 1.4.2: La réactivité des hydrocarbures aromatiques

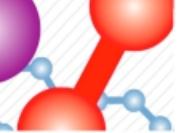
#### Halogenation du benzène:

- ❖ F<sub>2</sub> violent
- ❖ Cl<sub>2</sub>, Br<sub>2</sub> nécessite un catalyseur;
- ❖ I<sub>2</sub> endothermique

Ne réagit pas comme les alcènes



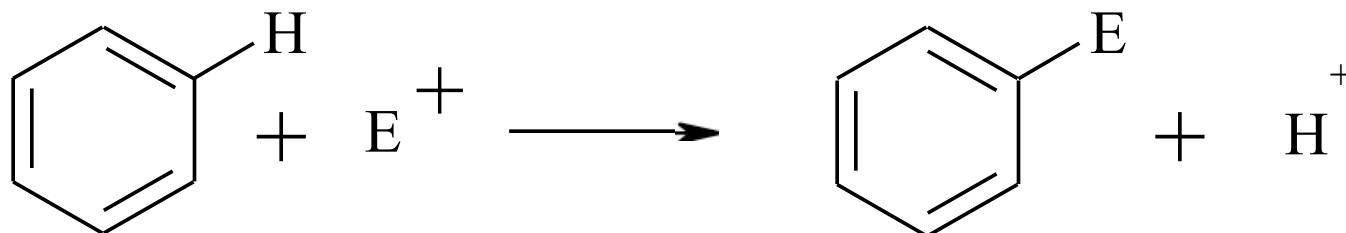
Substitution



## Partie 1.4 : Les Arènes

### Partie 1.4.2: La réactivité des hydrocarbures aromatiques

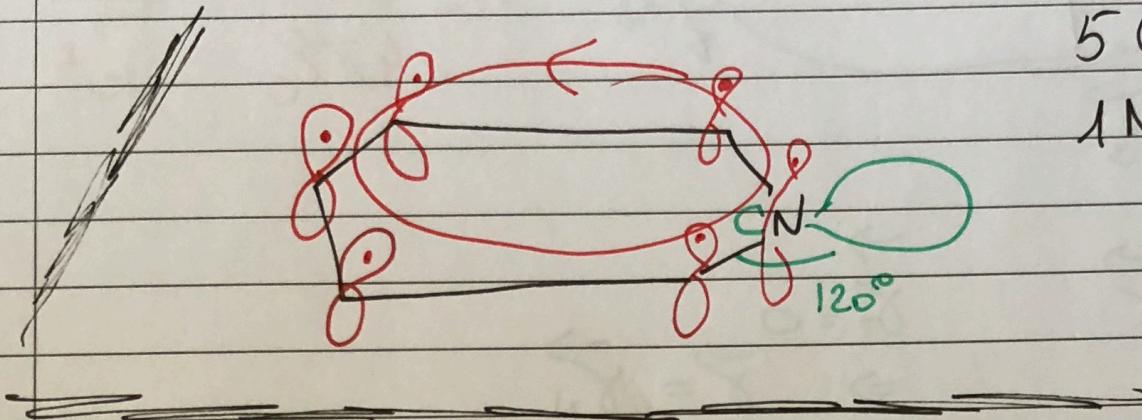
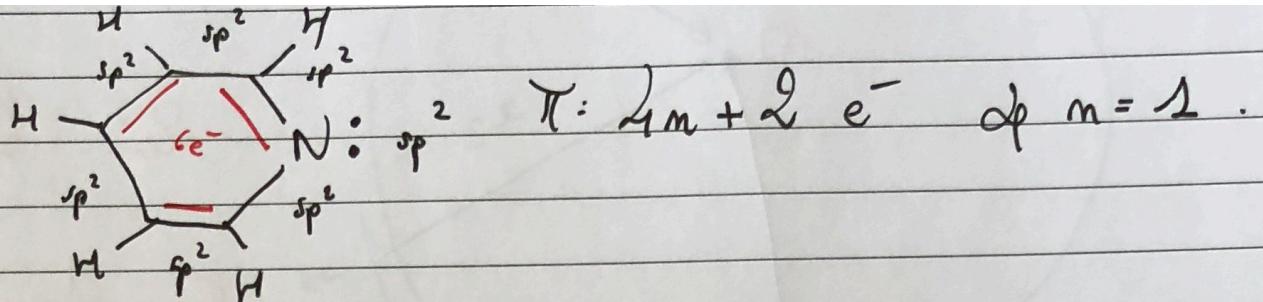
- La **Substitution Electrophile Aromatique ou SEAr**

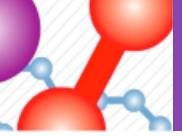


- Nécessite un **catalyseur**
- Substitution** (et non d'addition)
- Préserve l'**aromaticité**
- Attaque initiale par un réactif **électrophile**



p25



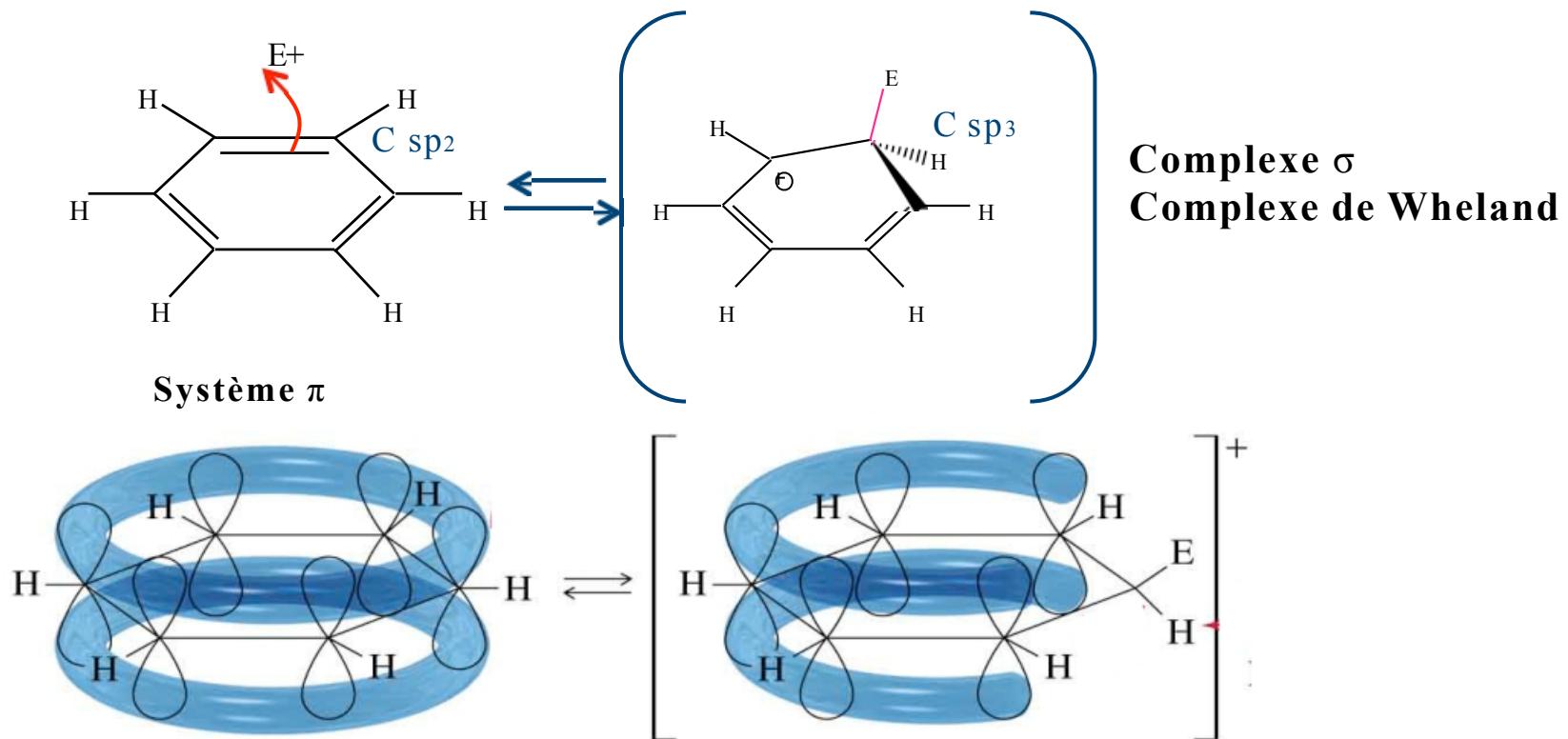


# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

- Le mécanisme réactionnel

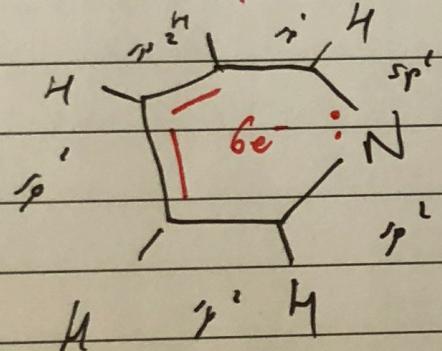
- Étape 1 : attaque de l'électrophile par les électrons du cycle aromatique



- perte d'aromaticité

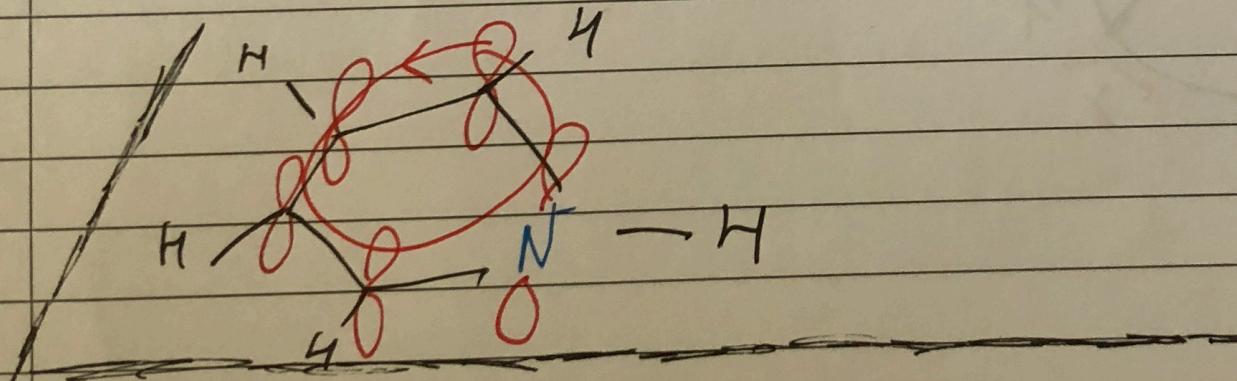
- Étape fortement endothermique

P<sup>26</sup>



$$\begin{array}{l} 1 C \rightarrow 1 e^- \\ 1 N \rightarrow 2 e^- \end{array}$$

$$\Rightarrow 6 e^-$$

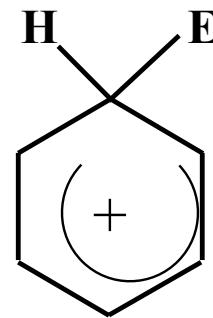
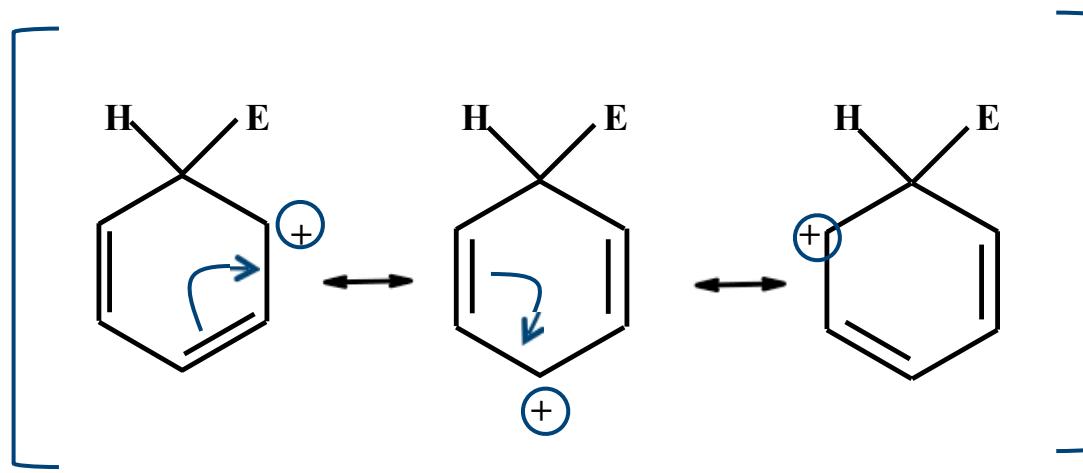




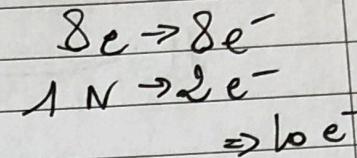
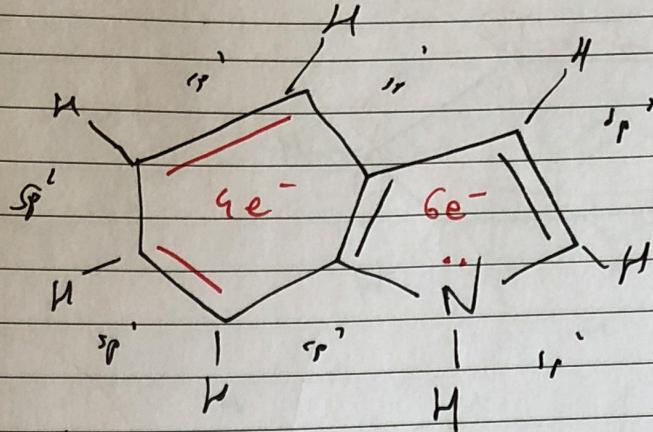
# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

### Le complexe sigma

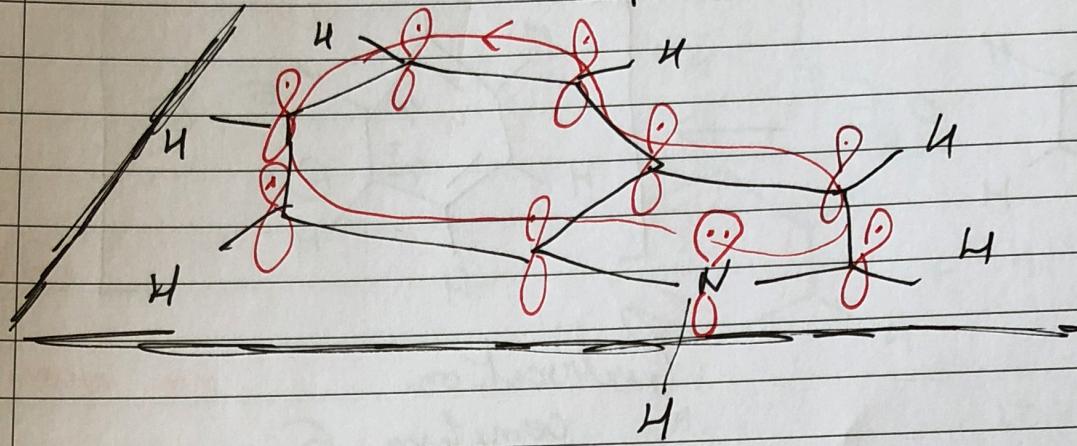


p27



$$\pi: 4m+2 \rightarrow m=2.$$

Indole



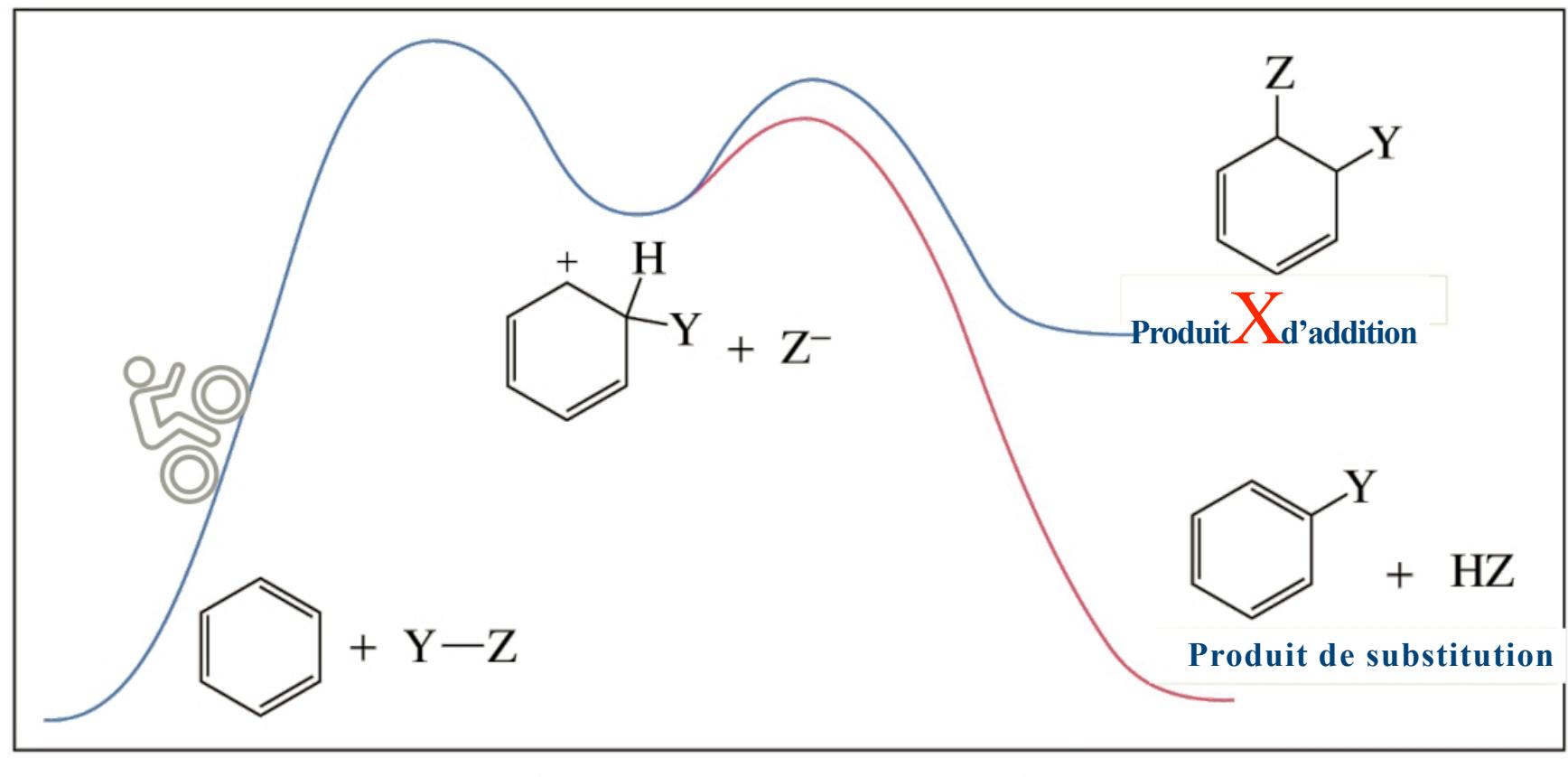


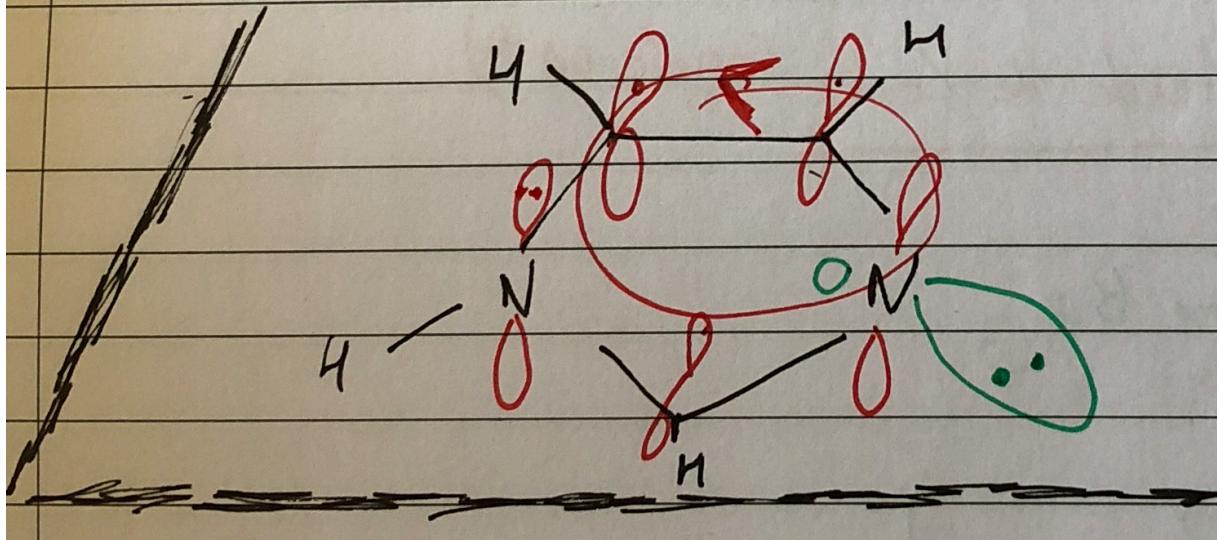
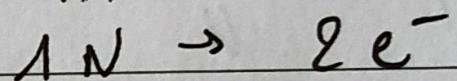
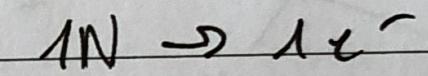
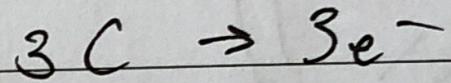
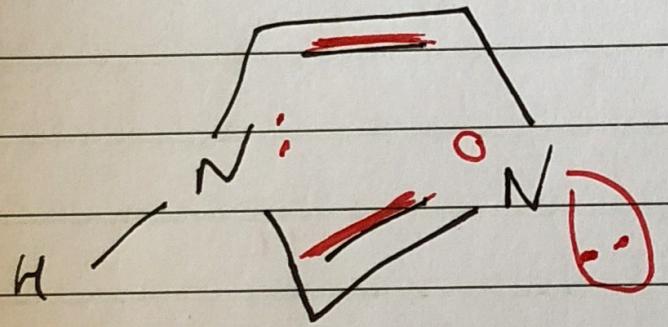
## Partie 1.4 : Les Arènes

### Partie 1.4.2: La réactivité des hydrocarbures aromatiques

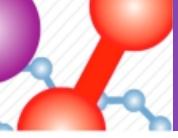
- Le mécanisme réactionnel

- Étape 2 : Perte d'un proton à partir du carbocation et ré-aromatisation





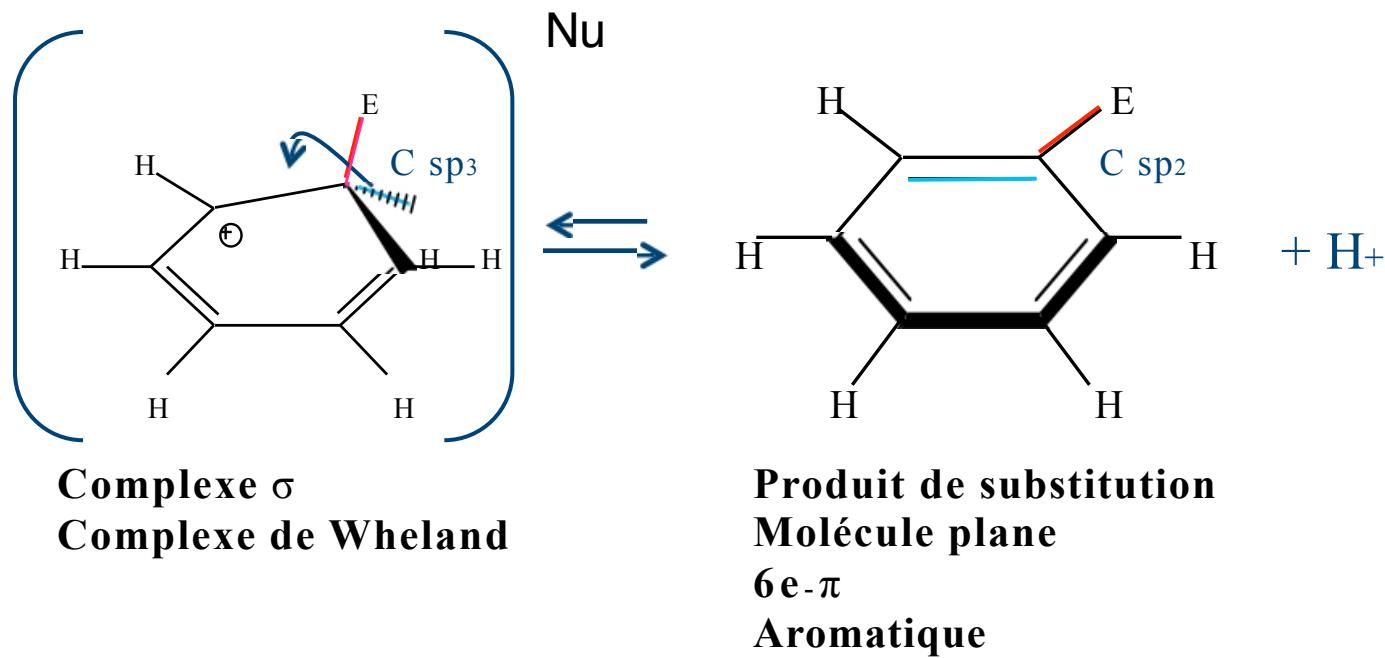
# Partie 1.4 : Les Arènes



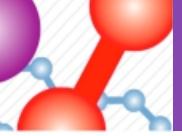
## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

### Le mécanisme réactionnel

#### Étape 2 : Perte d'un proton à partir du carbocation et ré-aromatisation

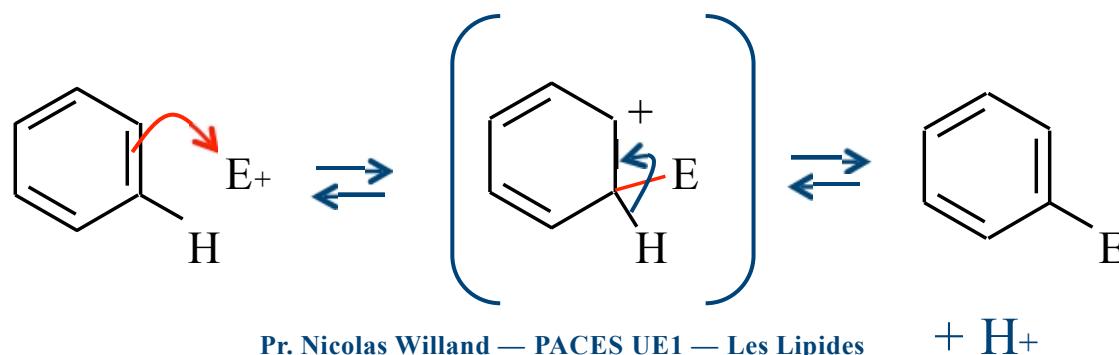
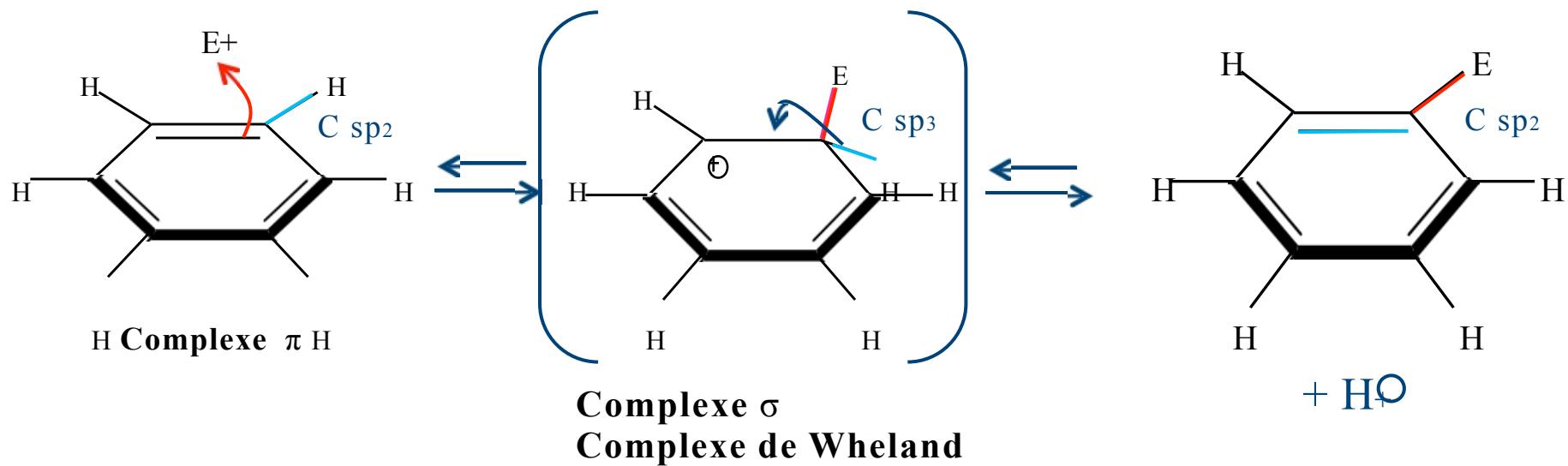


# Partie 1.4 : Les Arènes

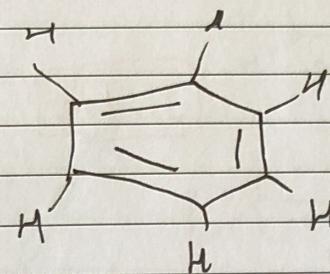
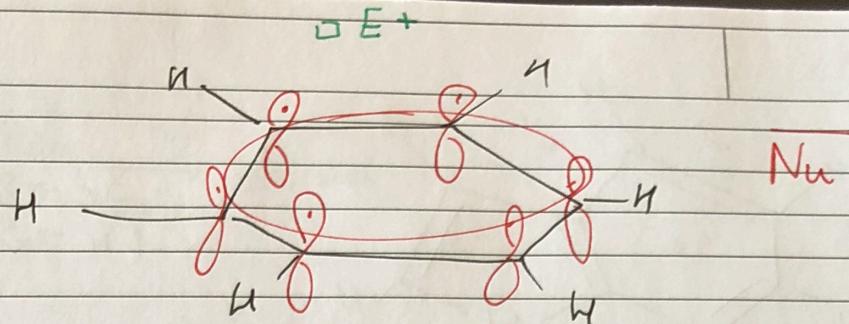


## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

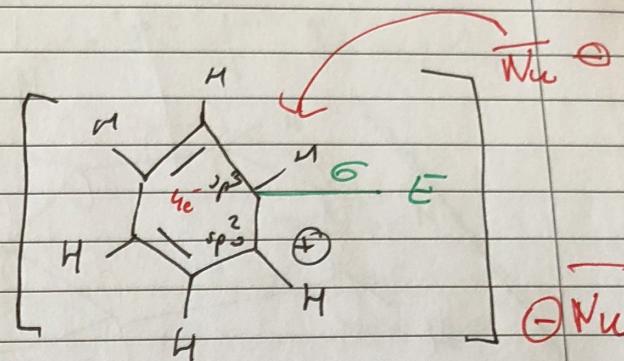
### Bilan



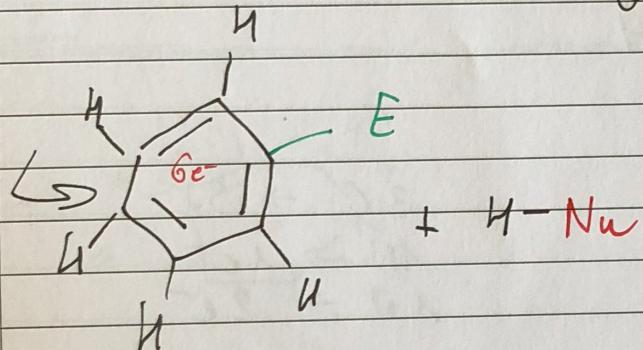
p30

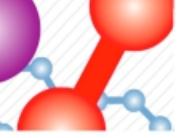


$E^+$



Carbocation : non aromatic  
complex  $\text{G}^-$   
 $\Rightarrow \text{O}^-$  stable





# Partie 1.4 : Les Arènes

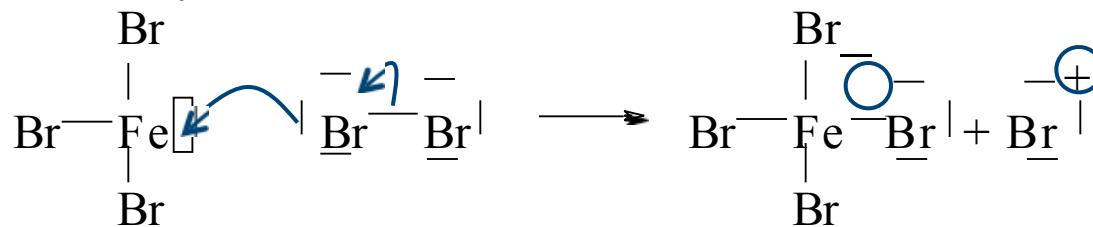
## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

### L'halogénéation du benzène

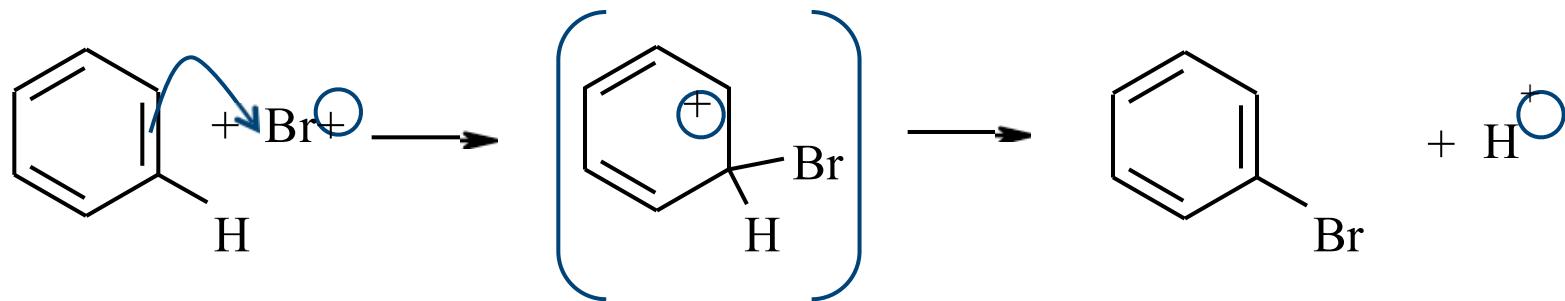
$Fe : [Arg] 4s^2 3d^6$

Pour augmenter le caractère électrophile des halogènes :

- utilisation de catalyseurs, acides de Lewis :  $AlBr_3, AlCl_3, FeCl_3, SbCl_5, BF_3\dots$

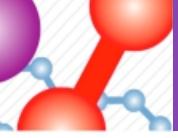


### Etape N°1: formation du carbocation



**Le chlore et le Brome** (mais pas le fluor qui est trop réactif) donnent des réactions de substitution en présence d'acides de Lewis.

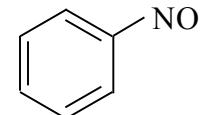
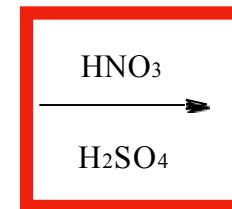
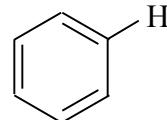




# Partie 1.4 : Les Arènes

## Partie 1.4.2: La réactivité des hydrocarbures aromatiques

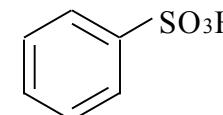
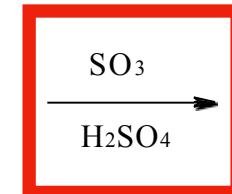
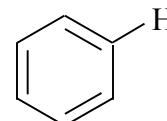
Nu



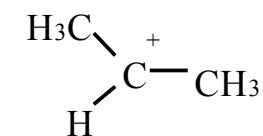
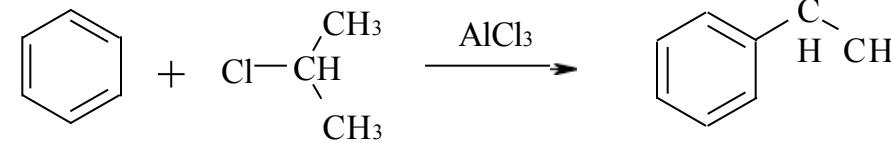
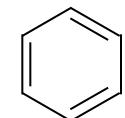
E+



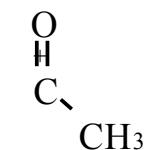
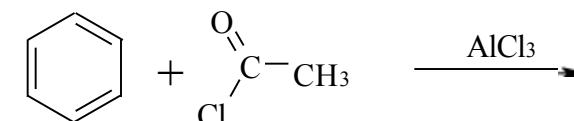
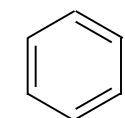
### Nitration



### Sulfonation

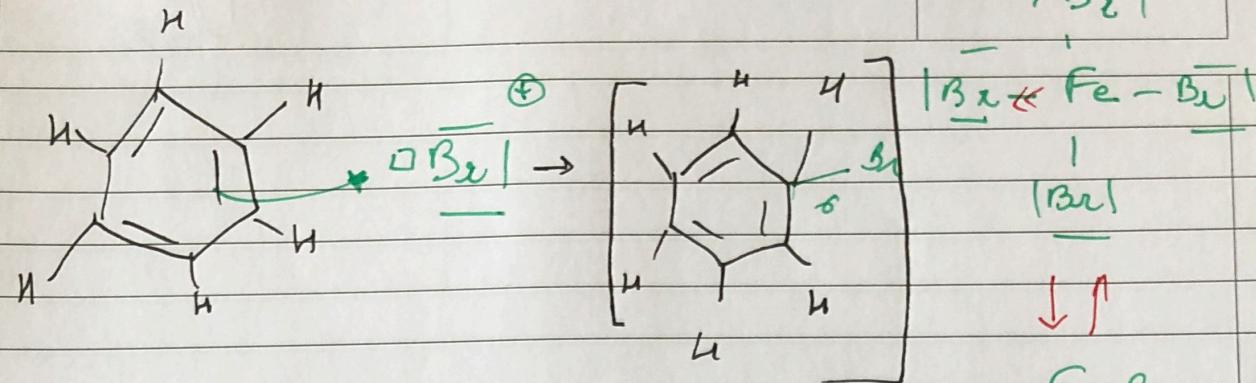


### Alkylation



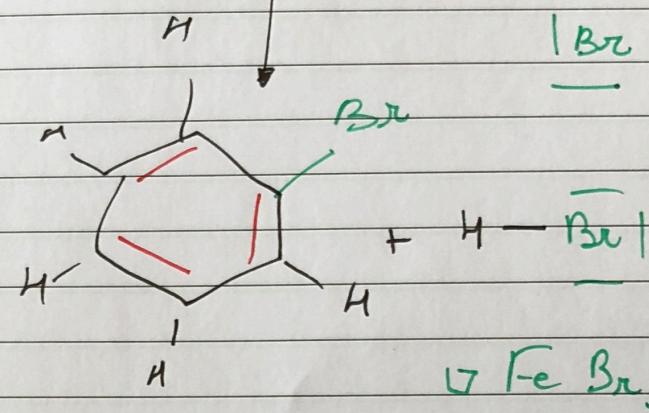
### Acylation

p 36

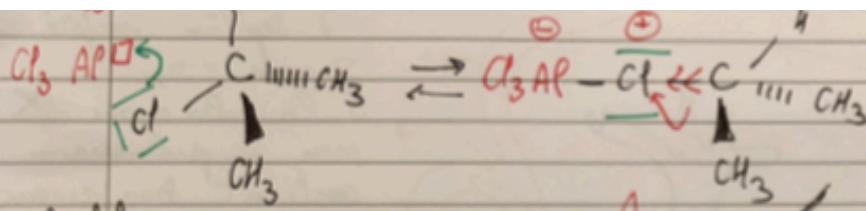


$|\text{Fe Br}_3|$

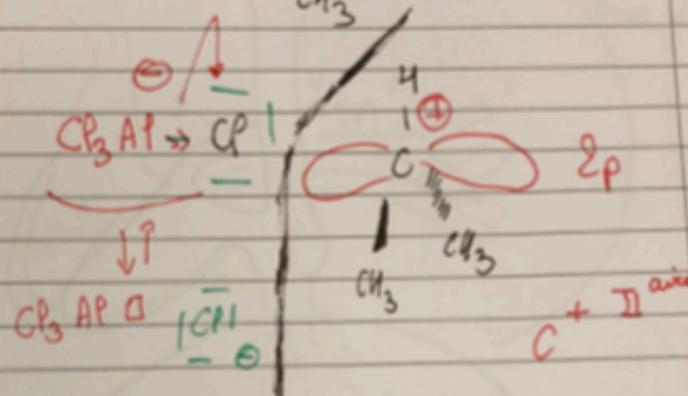
$|\text{Br}| \oplus$



$|\text{Fe Br}_3|$



2 chloro-p propane



Benzène

