Tut- Rentree

CHIMIE ORGANIQUE

Plan

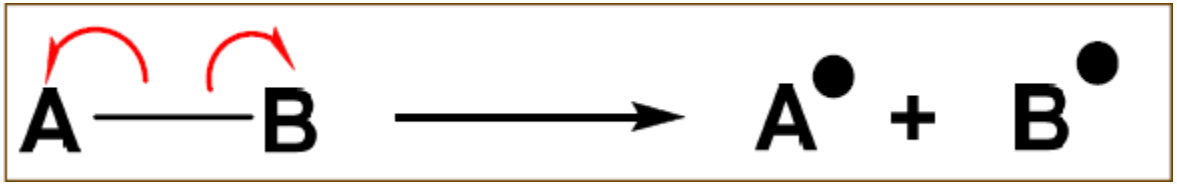
I. Substitutions Nucleophiles
II. Eliminations
III. Reactions acido-basiques

Reactions

- 2 types:
  - Homolytique
  - Heterolytique

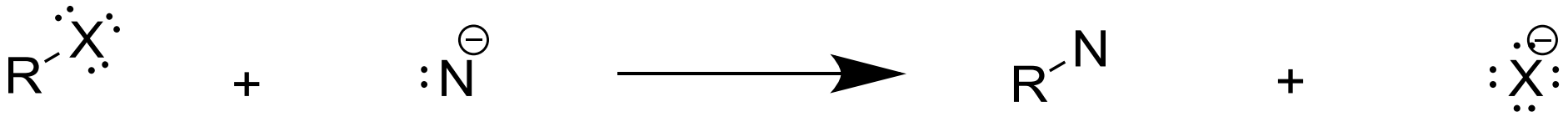
Reactions

- Homolytique



- Heterolytique

Substitution nucleophile



Nucleophilie

- Un nucleophile est une espece moleculaire qui a un exces d'electrons et qui va donc chercher a les partager. Il va etre a l'affut de charges positives.

- Comme exemples de bons nucleophiles, on a : -OH, -SH, -CN, -NH2, NH3, I- etc …

Exercice

- Classer ces molecules dans un ordre decroissant de nucleophilie:

(a) $\overset{\ominus}{O}H$ (b) $\overset{\ominus}{S}H$ (c) H_2S (d) H_2O

(e) NH_3 (f) $\overset{\oplus}{N}H_4$

Exercice

- Classer ces molecules dans un ordre decroissant de nucleophilie:

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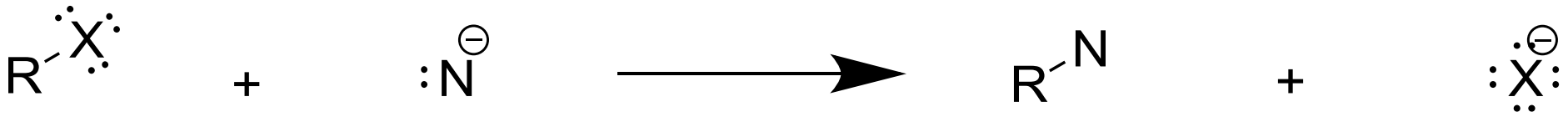
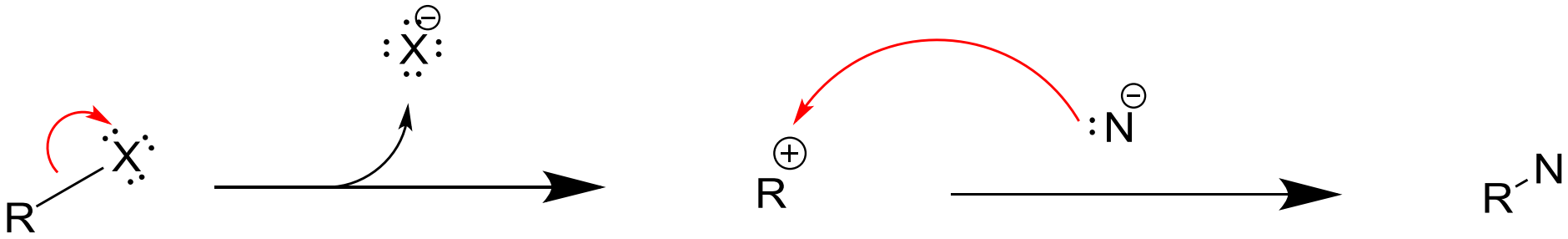
(e) NH_3 (f) $\overset{\oplus}{N}H_4$

(b) > (a) > (c) > (e) > (d) > (f)

Substitution nucleophile



SN1



SN1 (exemple)

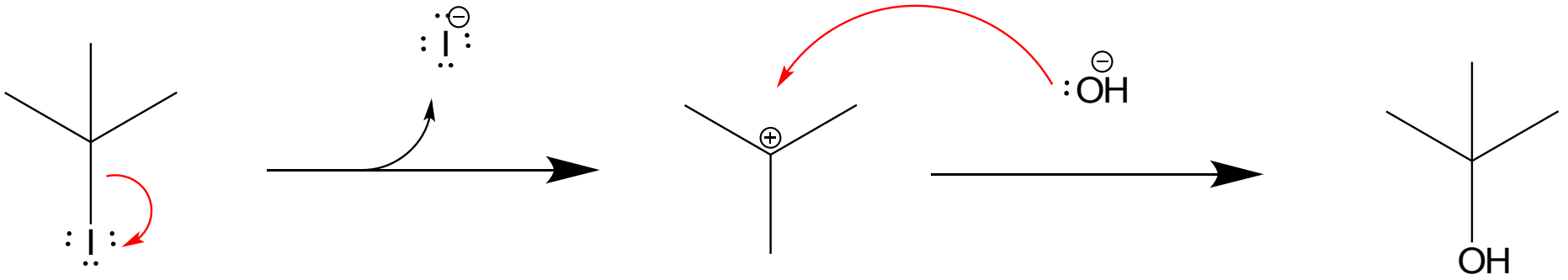
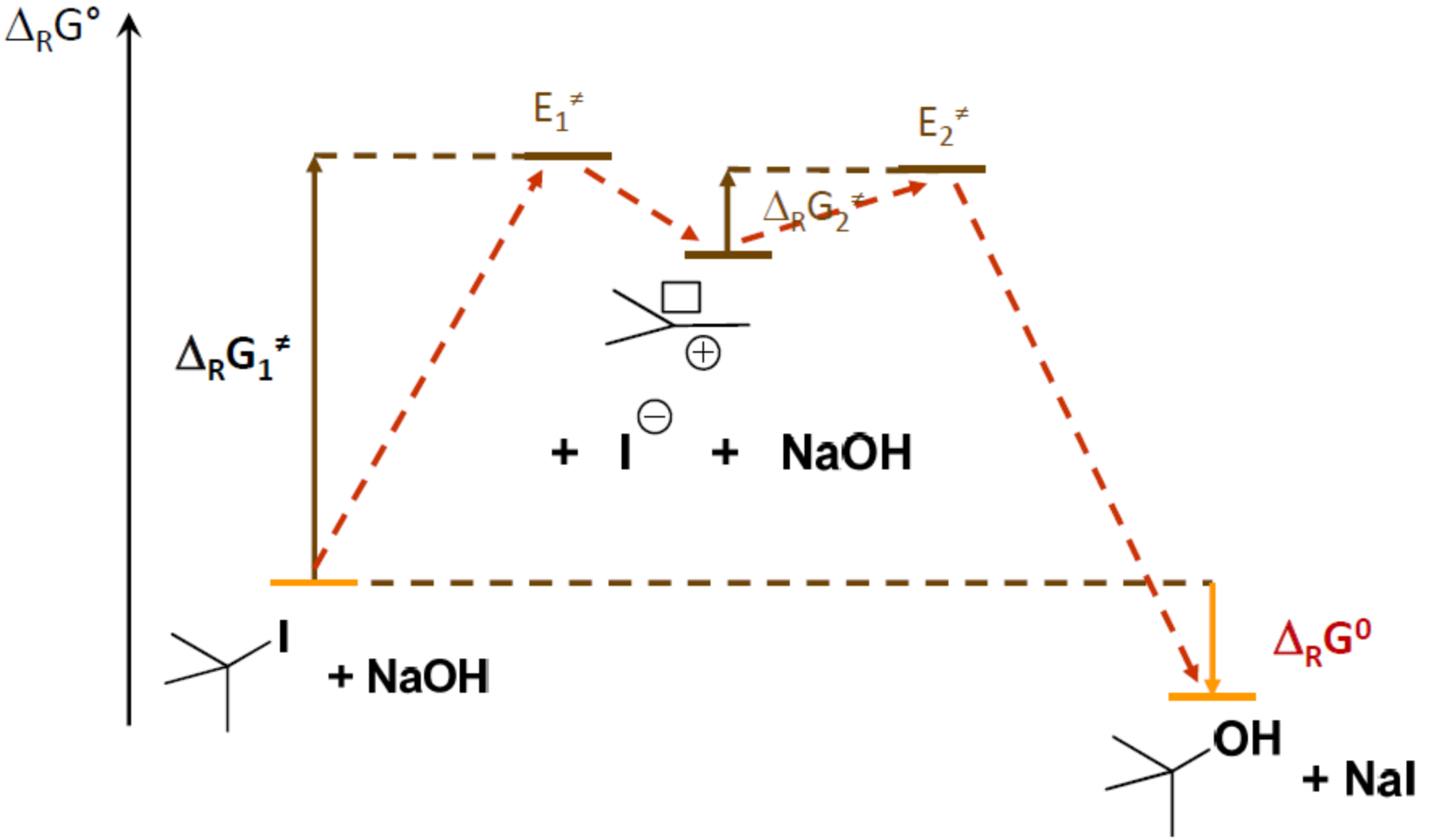


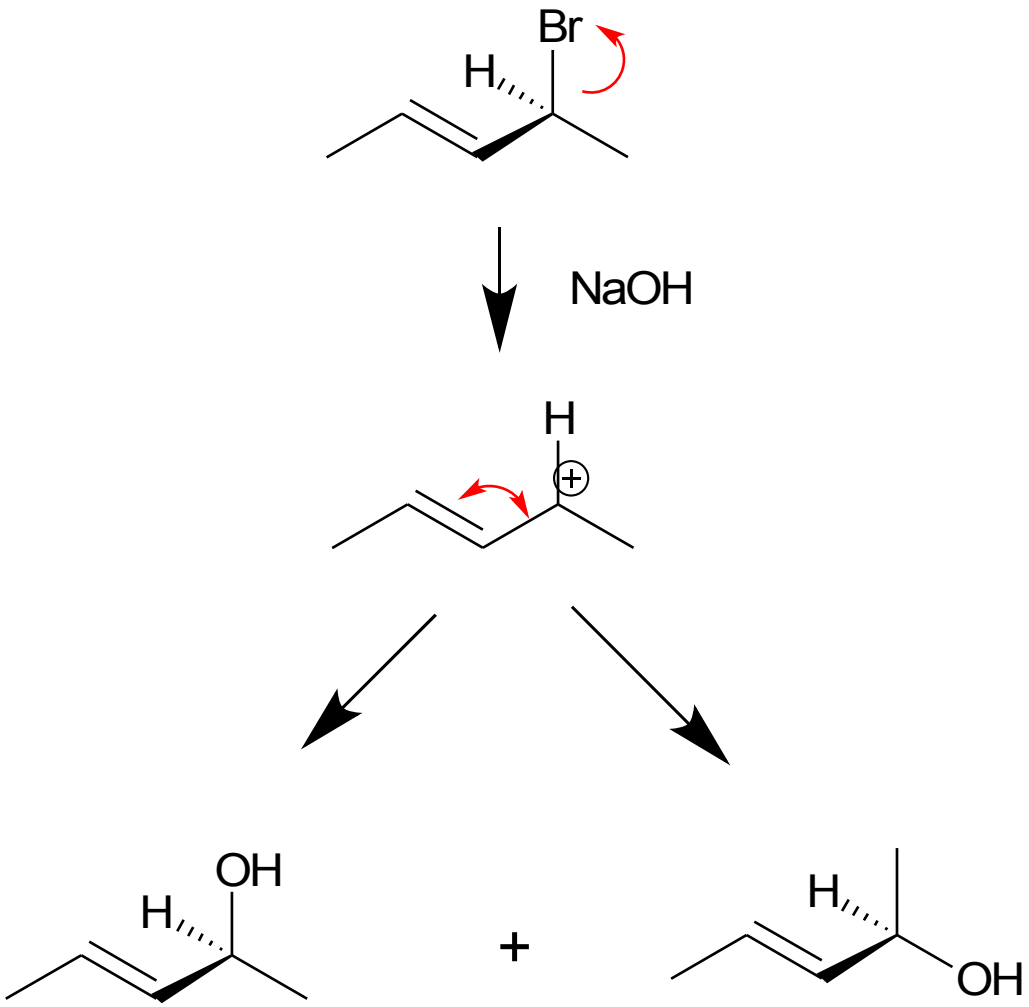
Diagramme energetique



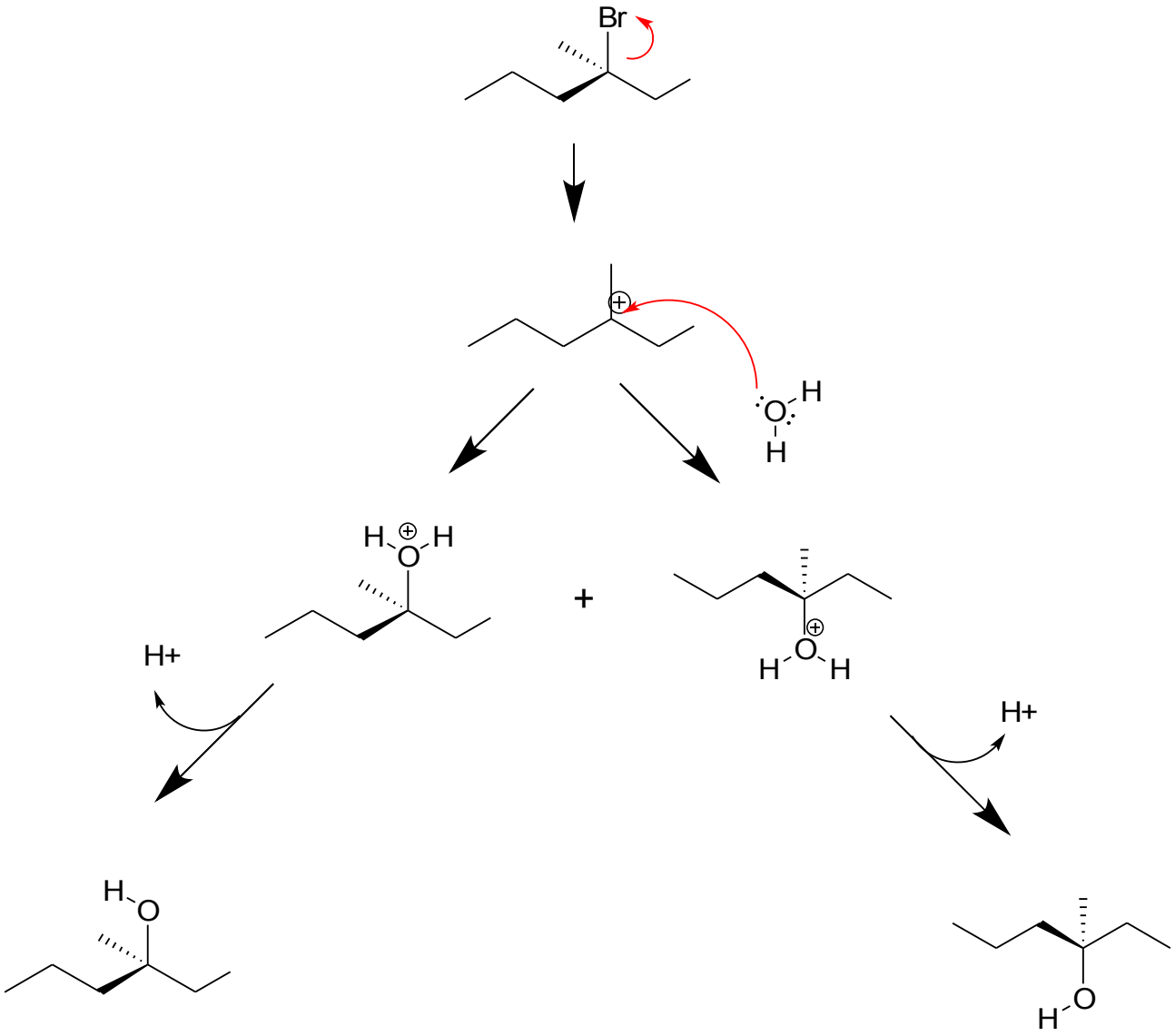
Postulat de Hammond

La structure d’un etat de transition se rapproche de l’etat intermediaire le plus proche en energie.

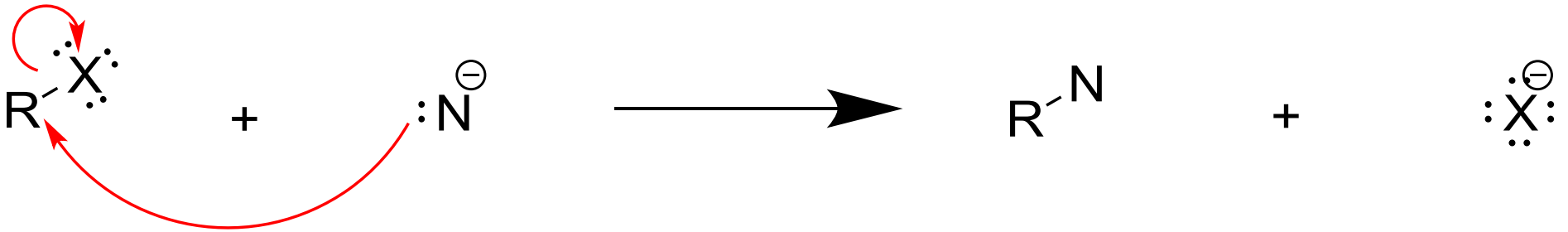
SN1 (stereochimie)



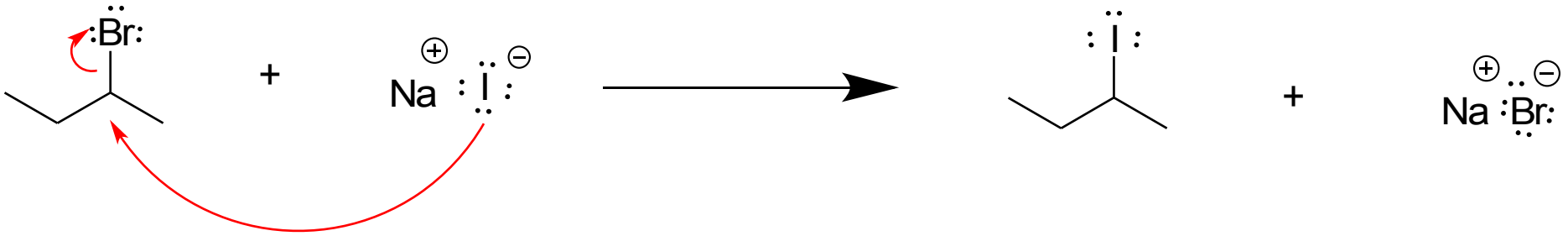
SN1 (stereochimie)



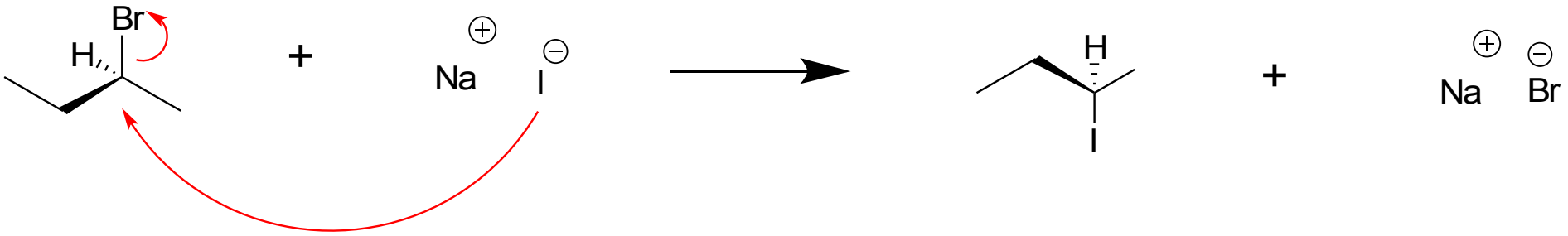
SN2



SN2

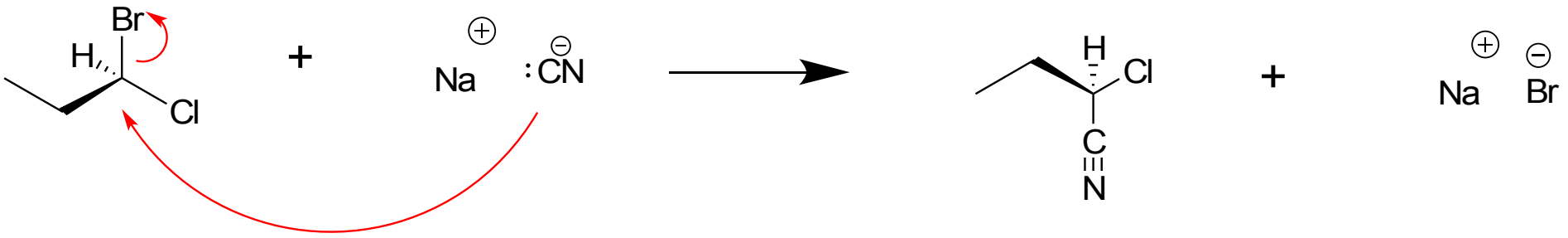


SN2 (stereochimie)

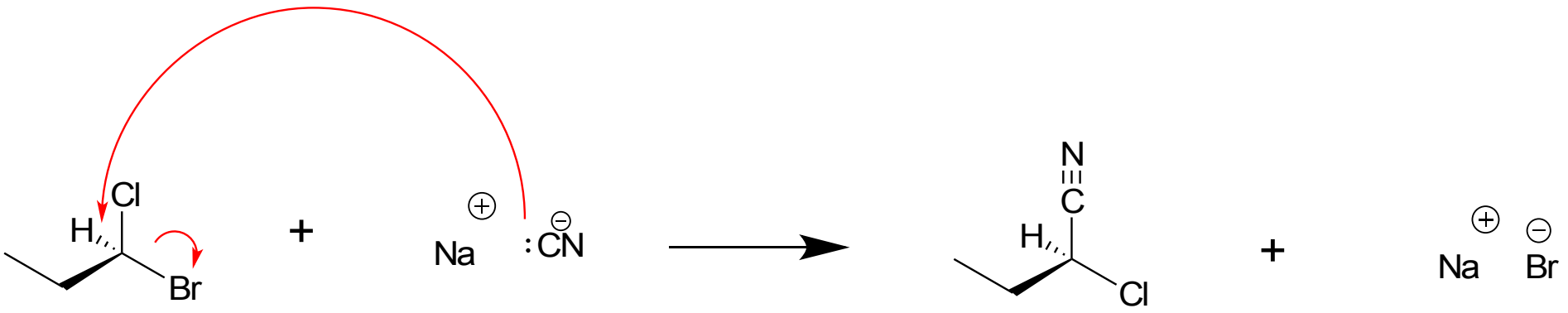


SN2 (stereochimie)

- Eg:



SN2 (stereochimie)

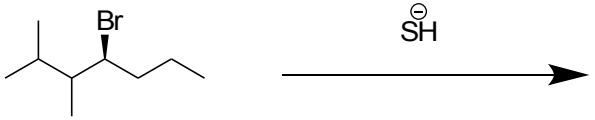


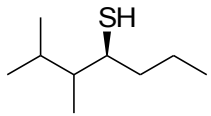
SN1 vs. SN2

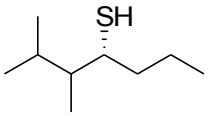
SN1	SN2
RX3 ou RX2 Bon nucleofuge Nuceophile moyen Solvant aprotique polaire	RX0, RX1 ou RX2 Nucleofuge moyen Bon nucleophile Solvant protique polaire

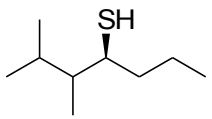
Exercice

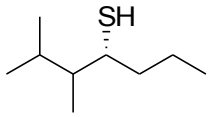
- Quel est le produit majoritaire de la reaction suivante?

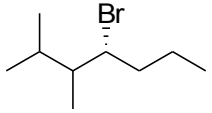


(a) 

(b) 

(c) 

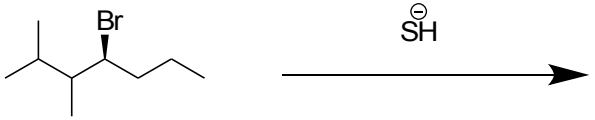


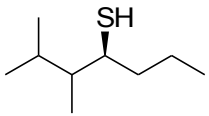
(d) 

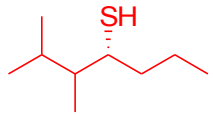
(e) Aucune reponse n'est correcte.

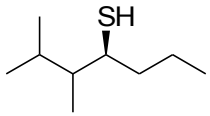
Exercice

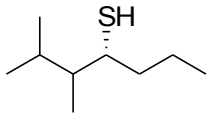
- Quel est le produit majoritaire de la reaction suivante?

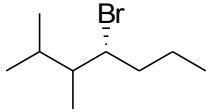


(a) 

(b) 

(c) 



(d) 

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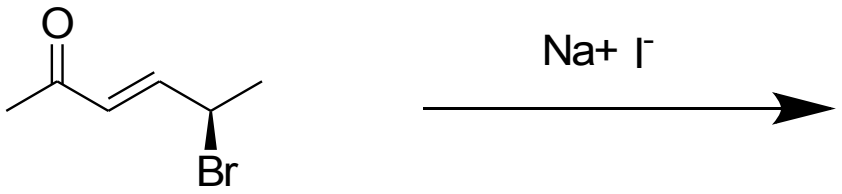
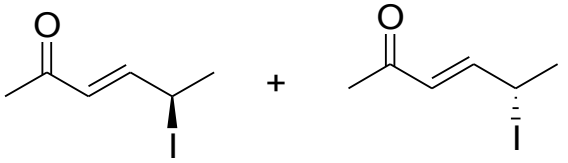
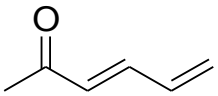
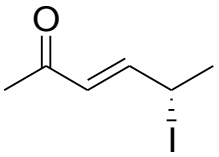
QCM

- Quel est le produit majoritaire de la reaction ci-dessous?



(a) 

(b) 

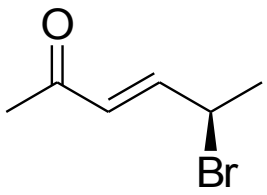
(c) 

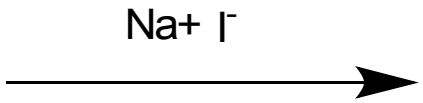
(d) (*R*,*E*)-5-iodohex-3-en-2-one

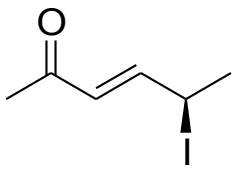
(e) Toutes les reponses sont fausses.

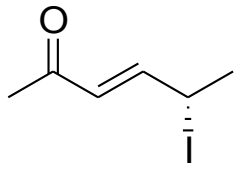
QCM

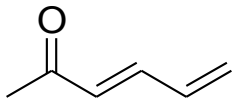
- Quel es le produit majoritaire de la reaction ci-dessous?

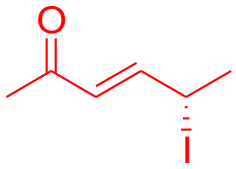




(a) 

+ 

(b) 

(c) 

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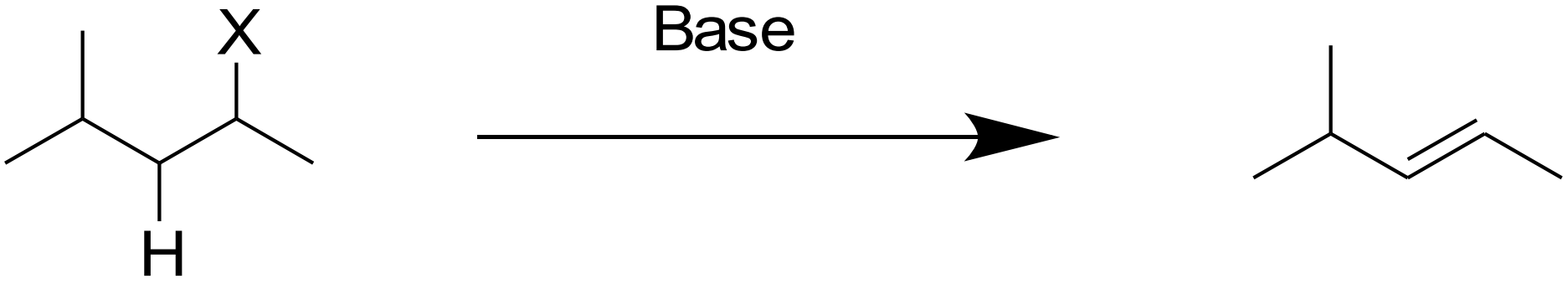
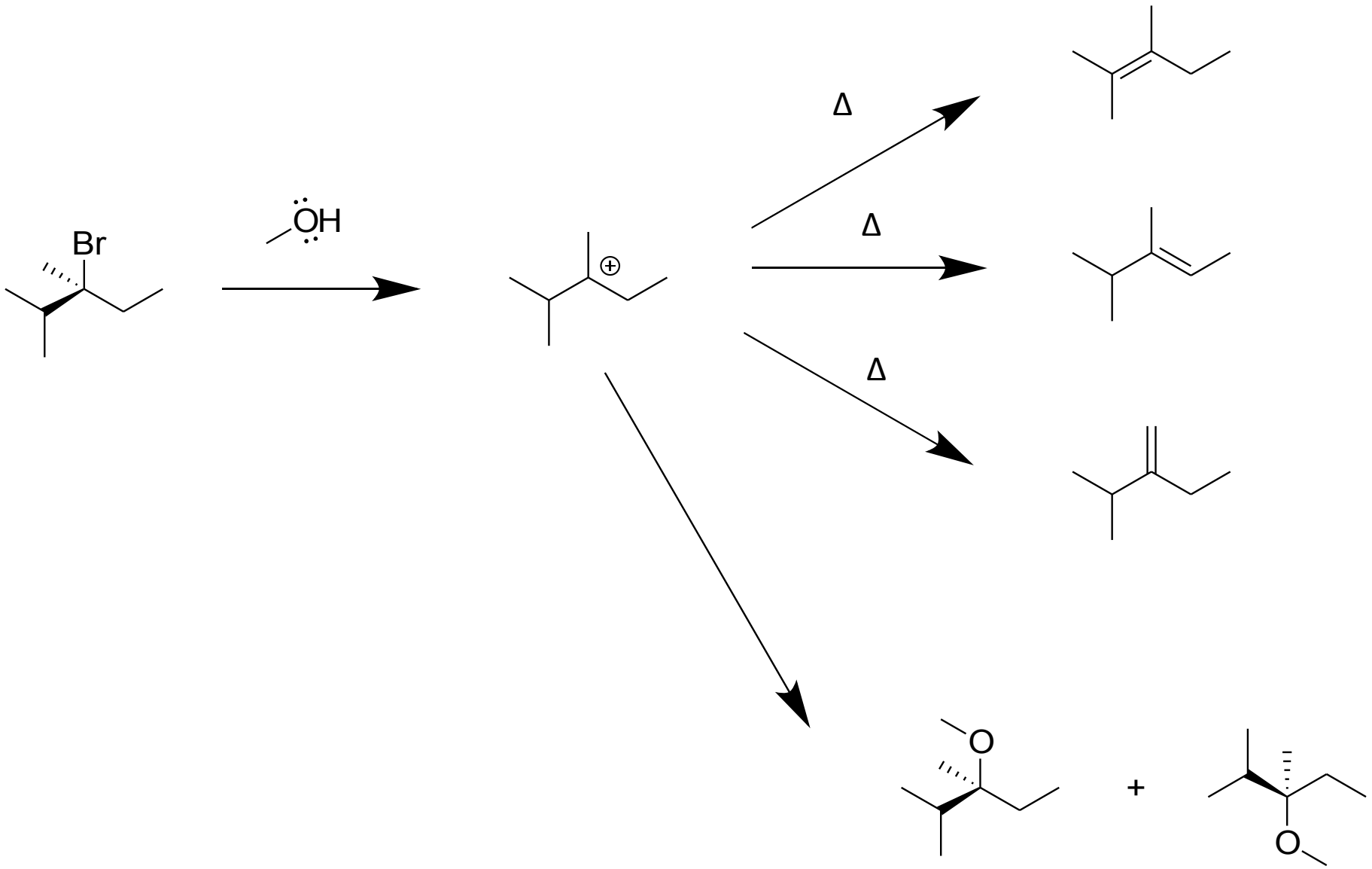
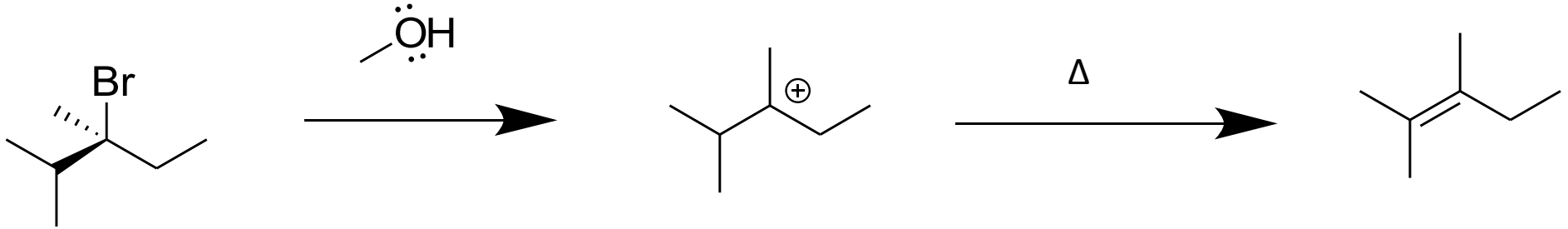
Elimination



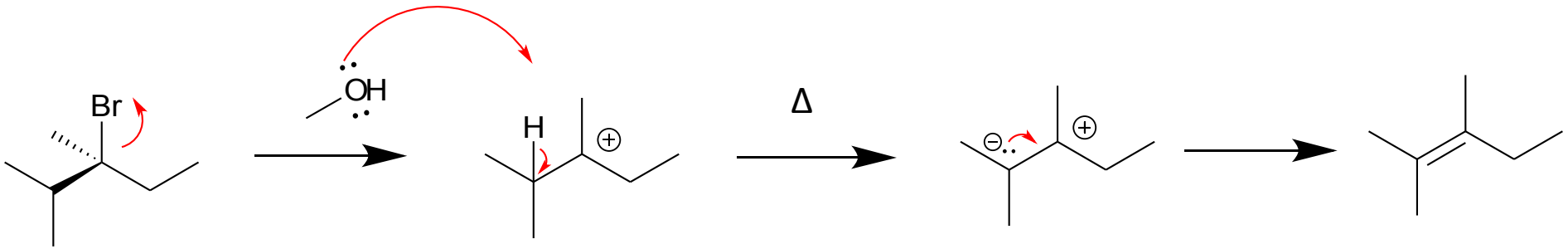
E1



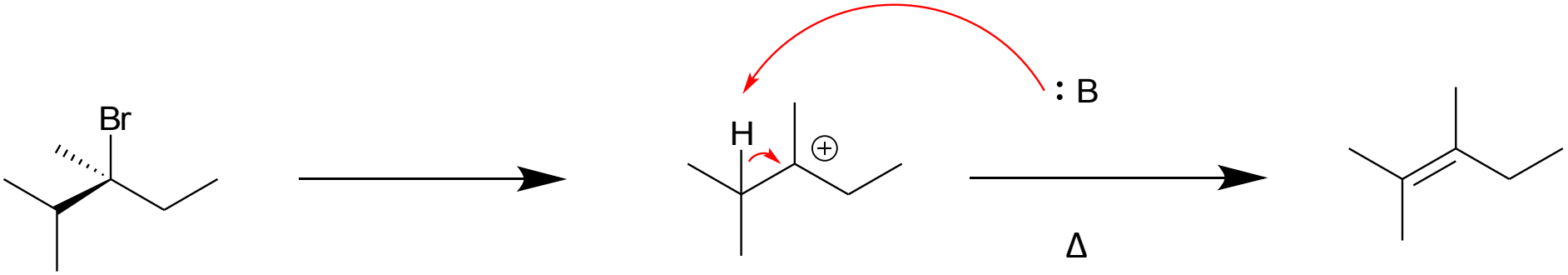
E1



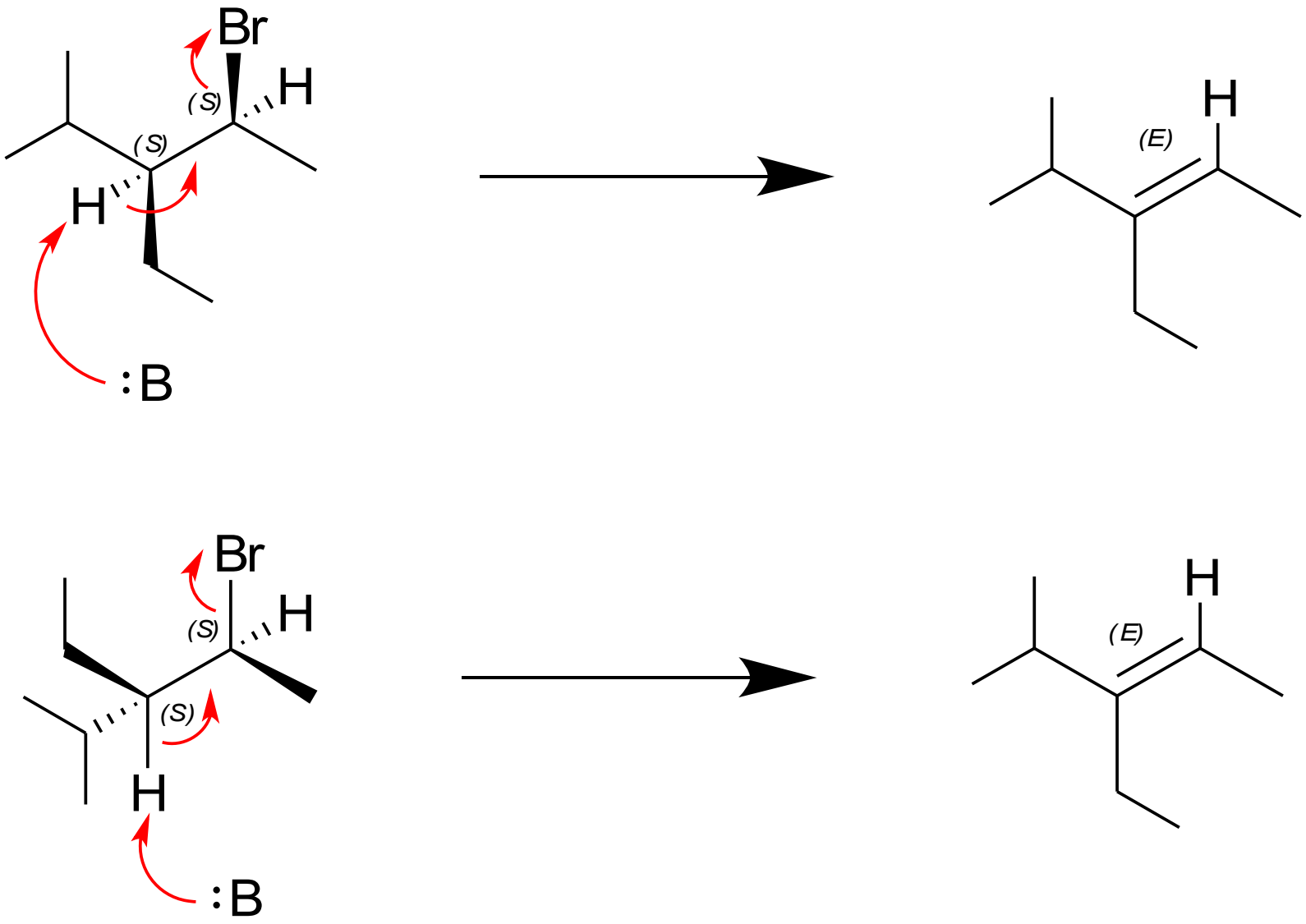
Mecanisme



E1 : Mecanisme



E2

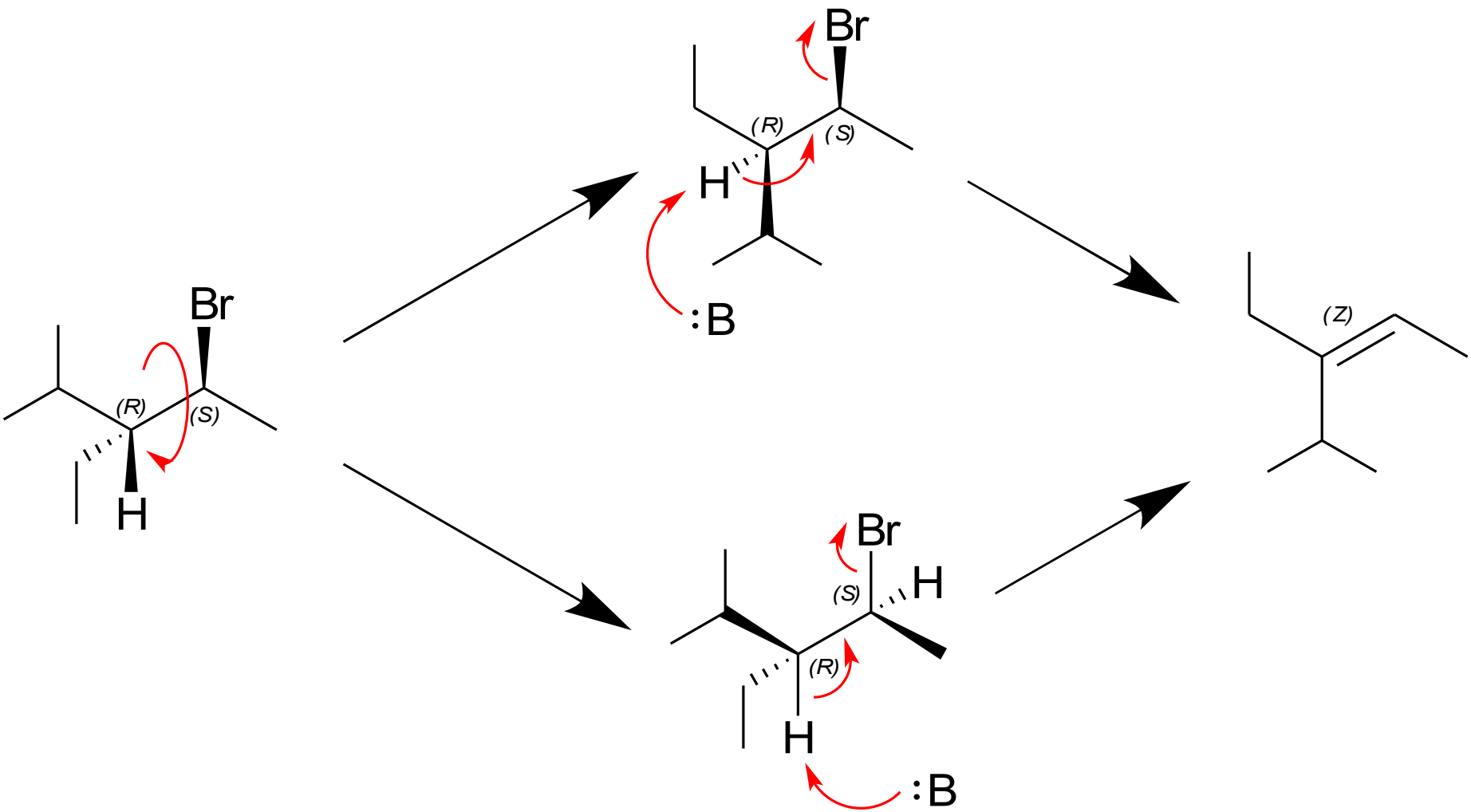


E2

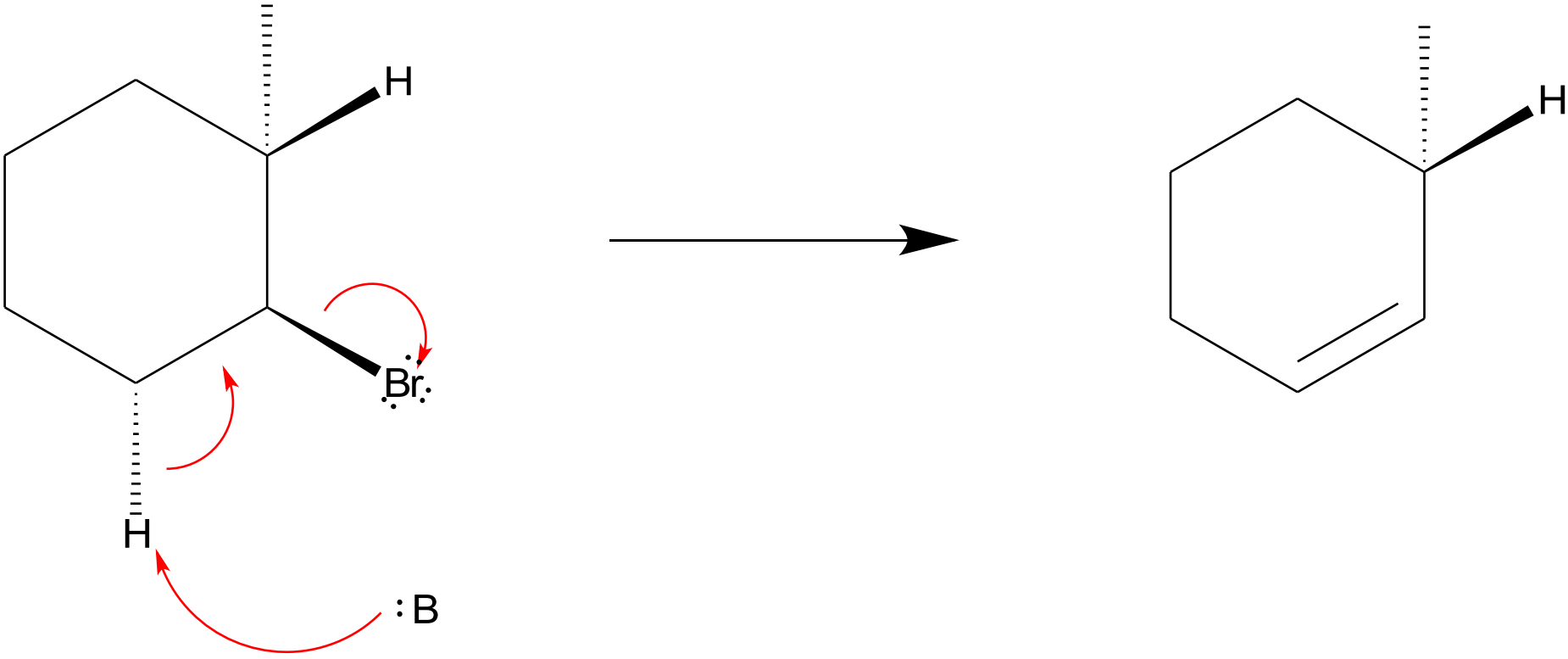
- Exemples de bases fortes:

LDA, t-ButOK, -OH, ButLi, NH2-

E2



E2

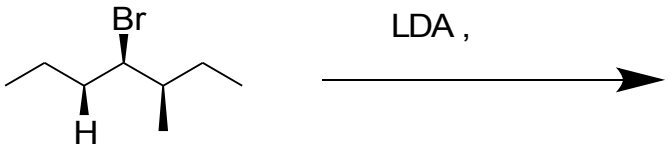


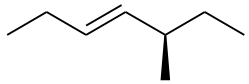
E1 vs. E2

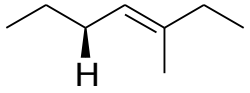
E1	E2
· Stabilite du carbocation (tertiare ou mesomerie) · Chauffage · Base faible · Bon nucleofuge	· Base forte · Nucleofuge moyen · Chauffage (preferable) · Proton en anti

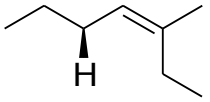
Exercice

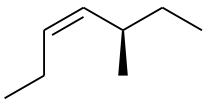
- Quel est le produit majoritaire de la reaction suivante?



(a) 

(b) 

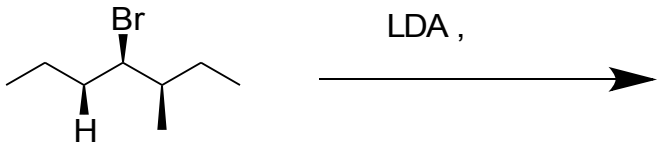
(c) 

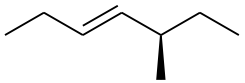
(d) 

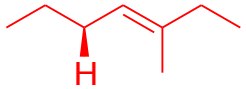
(e) Aucune reponse juste.

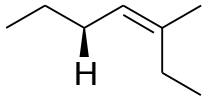
Exercice

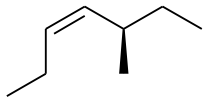
- Quel est le produit majoritaire de la reaction suivante?



(a) 

(b) 

(c) 

(d) 

(e) Aucune reponse juste.

Reactions Acide/Base

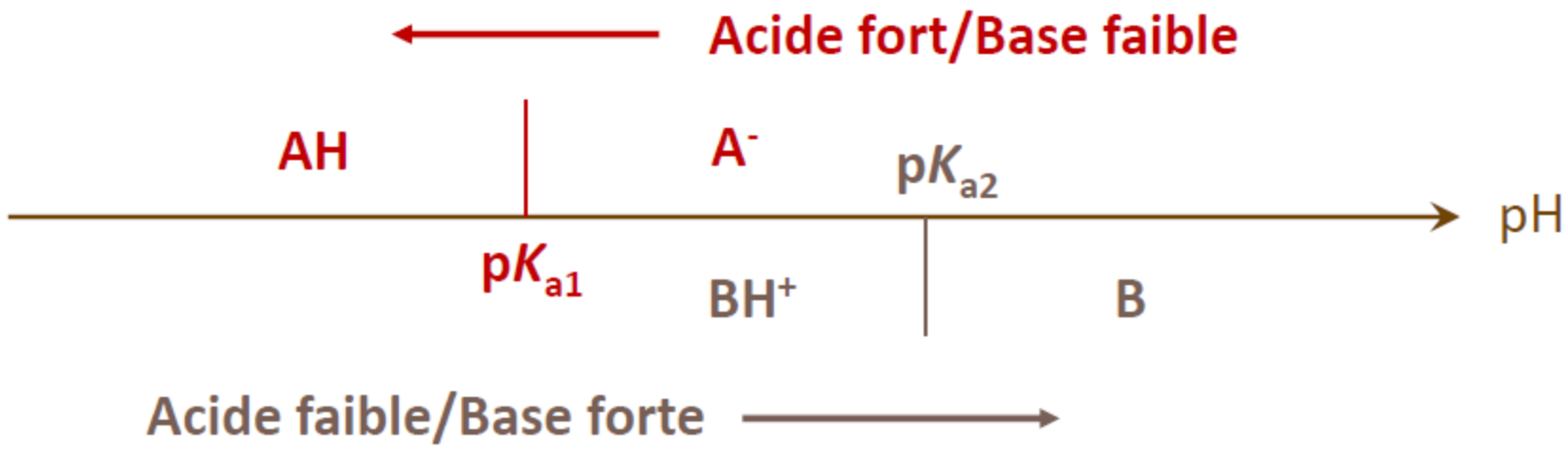
- On distingue:

  - rxn acido-basiques selon Lewis
  - rxn acido-basiques selon Bronsted

Reactions A/B selon Bronsted

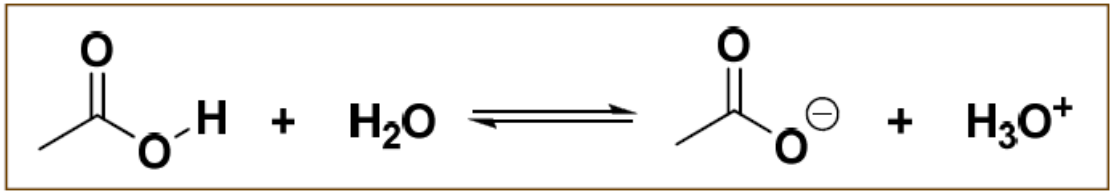
- Soit les couples AH/A- et BH+/B avec les pKa respectifs pKa1 et pKa2.
- Si pKa1 < pKa2 la reaction sera favorisee.

Diagramme de prédominance des espèces :



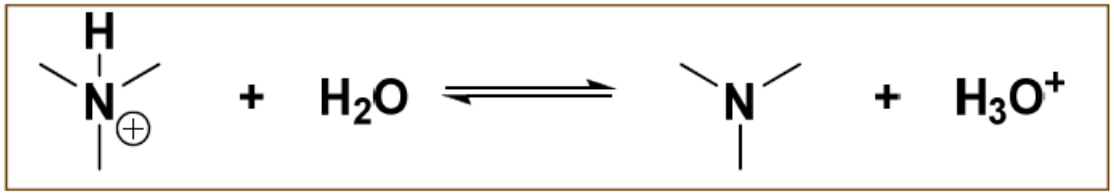
Exemple

Couple $CH_3CO_2H/CH_3CO_2^-$

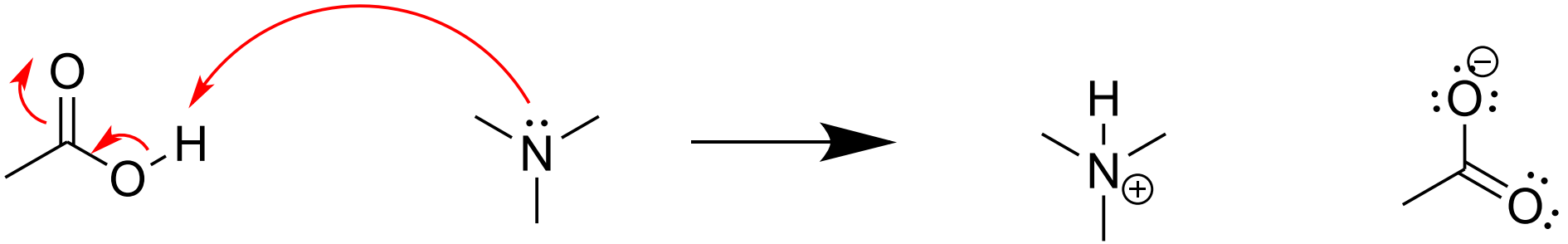


K_{a1}

Couple $(CH_3)_3NH^+/(CH_3)_3N$

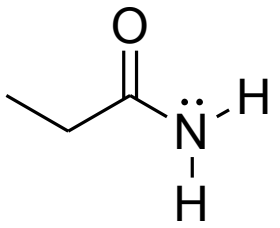


K_{a2}

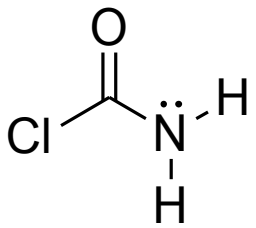


Exercice

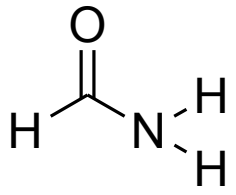
- Classer par ordre d'acidite decroissante les molecules suivantes:



(a)



(b)



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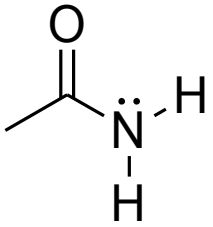
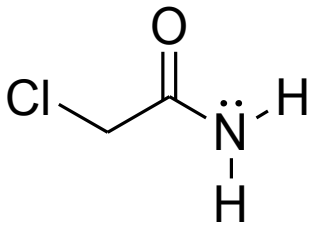


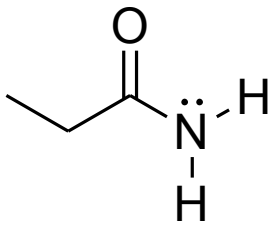
(d)



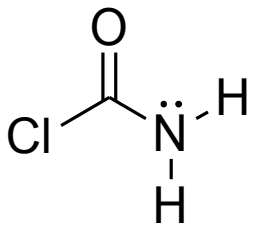
(e)

Exercice

- Classer par ordre d'acidite decroissante les molecules suivantes?



(a)



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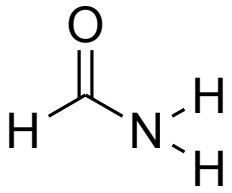
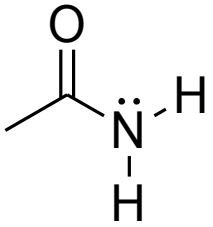


(c)



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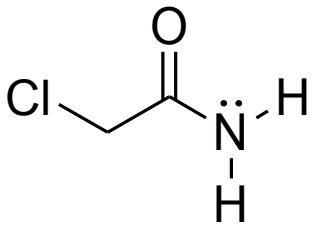
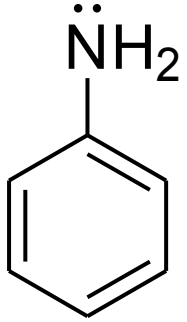


(e)

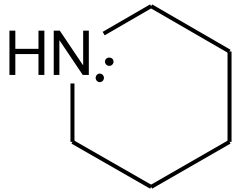
(b) > (e) > (c) > (d) > (a)

Exercice

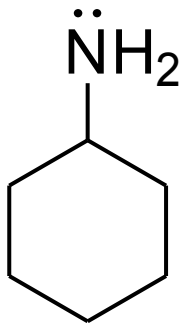
- Classer par ordre de basicite decroissante les molecules suivantes:



(a)



(b)



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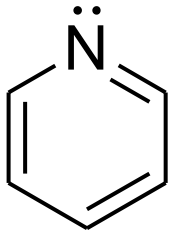
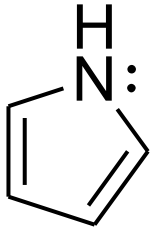


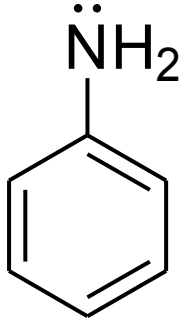
(d)



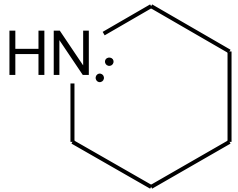
(e)

Exercice

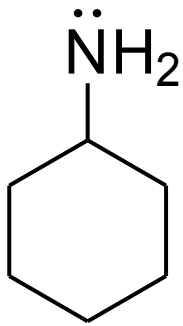
- Classer par ordre de basicite decroissante les molecules suivantes:



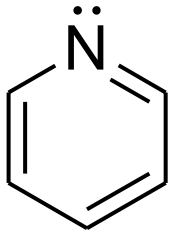
(a)



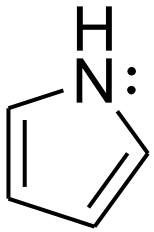
(b)



(c)



(d)

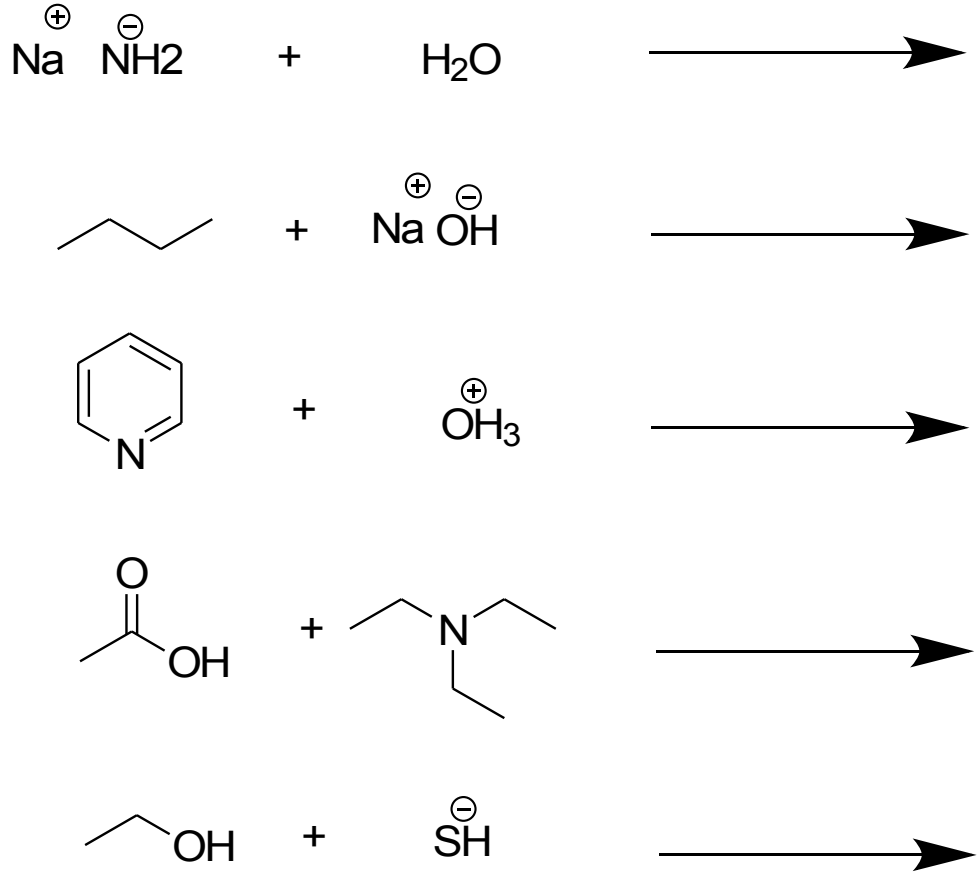


(e)

(b) > (c) > (d) > (a) > (e)

Exercice

- Parmi les reactions ci-dessous, lesquelles vont conduire a la formation de produits?



Exercice

- Parmi les reactions ci-dessous, lesquelles vont conduire a la formation de produits?