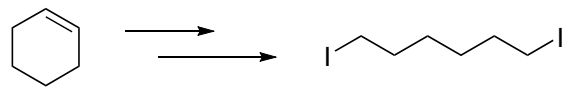
1)



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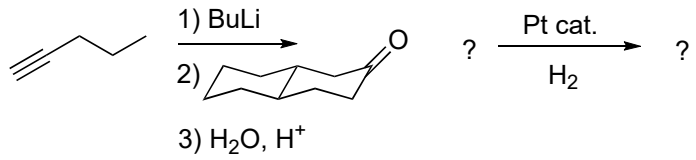

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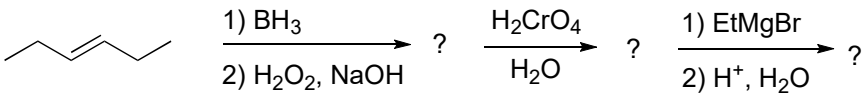
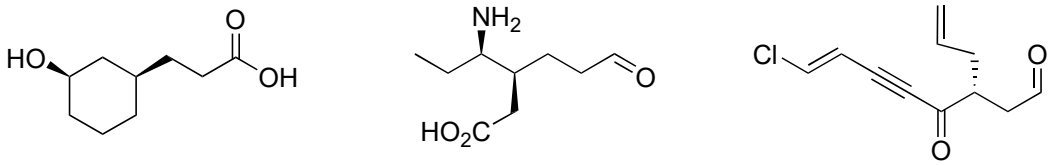


4) Donner le nom systématique IUPAC des molécules suivantes:



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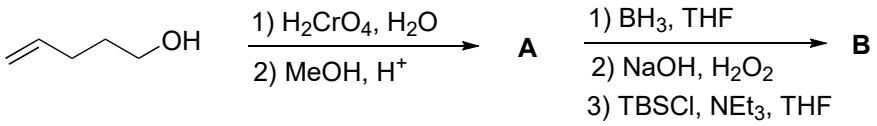
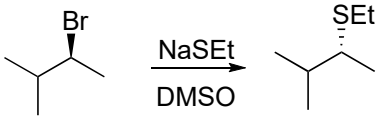


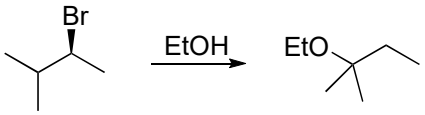
6)

Pour les réactions suivantes:
1) Proposez un mécanisme.
2) Pour chaque étape de votre mécanisme, indiquer l'interaction orbitalaire qui déclenche l'étape (orbitale x de atome/liaison 1 réagit avec orbitale y de atome/liaison 2, par exemple: nO vers σ*C-O, un dessin n'est pas demandé, n = paire d'électron, π = pi, σ = sigma, p = orbitale p).
3) Dessiner un profil énergétique approximatif pour les réactions

(1)



(2)



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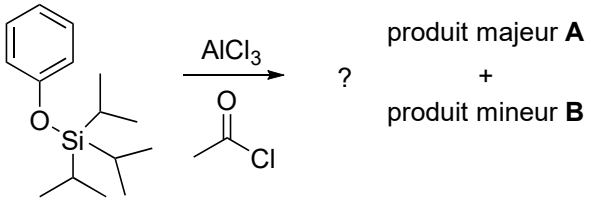

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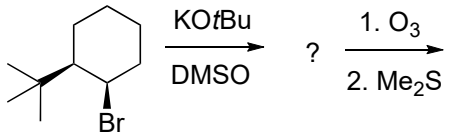
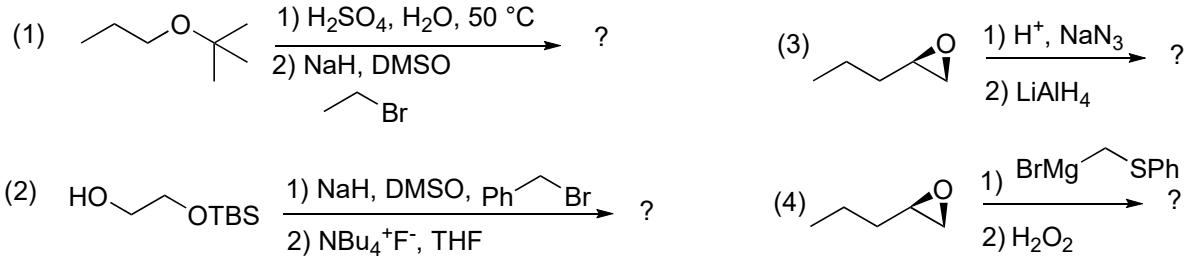


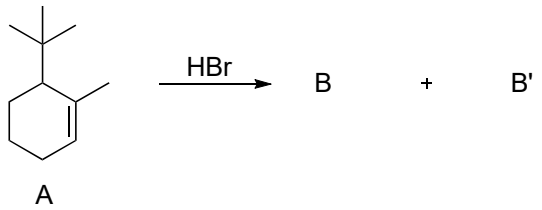
9)

Donner les produits et les mécanismes des réactions suivantes.



10) Représenter le diagramme d'énergie potentielle de la rotation autour de la liaison C2-C3 du 2-méthylbutane. Indiquer qualitativement comment le diagramme changerait dans le cas du 2-chlorobutane en vous basant sur des effets stériques et des interactions orbitalaires (indication: considérez que le chlore est plus petit qu'un groupe méthyl et plus électronégatif).

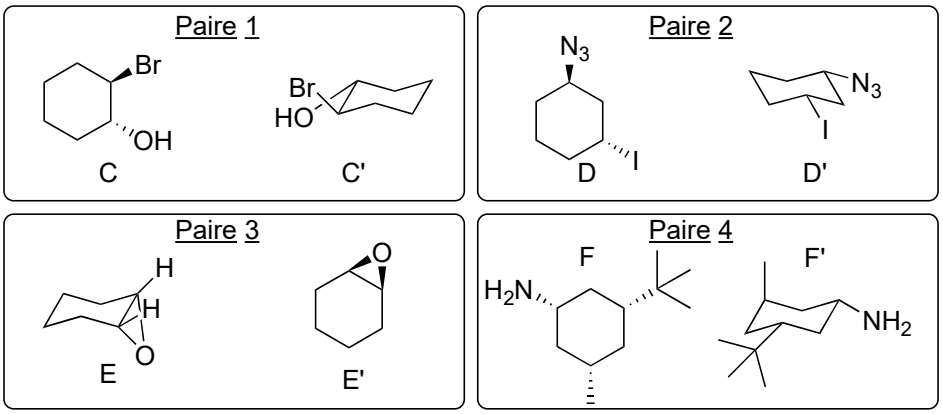
11)



A) Dessiner la forme R de la molécule A.
B) Proposer un mécanisme pour la formation de B et B'. Représenter en conformation chaise les molécules B et B'. Quelle est la relation entre B et B' ?
C) Quel produit est le plus stable ?

12)

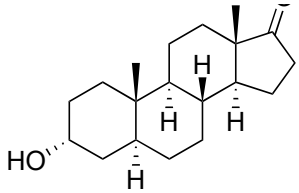
A) Pour chaque paire, donner la relation entre les deux composés (identiques, énantiomères ou diastéréoisomè res).
B) Déterminer la stéréochimie R ou S de chaque centre chiral.
C) Donner la nomenclature du composé C.



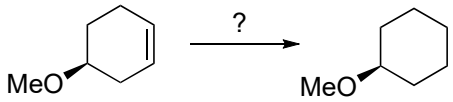
13)

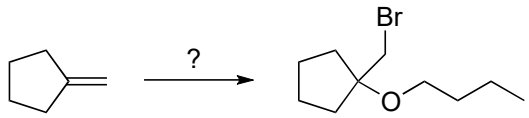
Dessiner la conformation favorisée de l'androstérone.

O



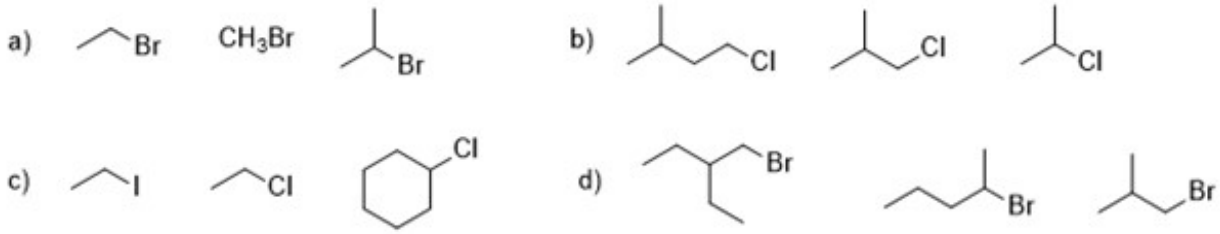
14) Donner les réactifs et les mécanismes réactionnels des transformations suivantes.



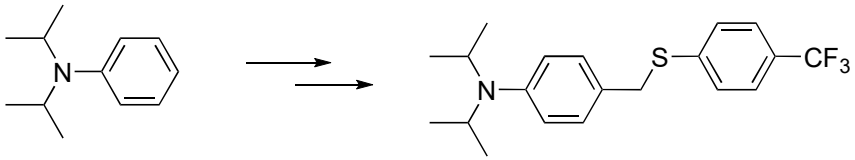


racémique

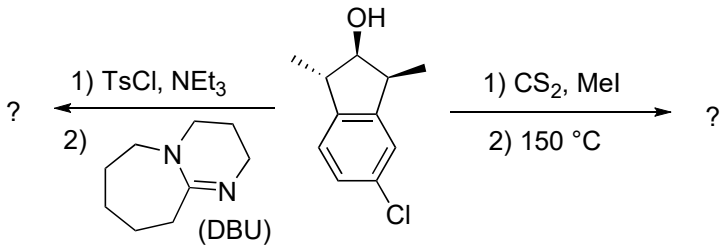
15) Classer les différentes familles de molécules ci-dessous par ordre de réactivité croissante vis-vis d'une ré action SN2. Justifier votre réponse



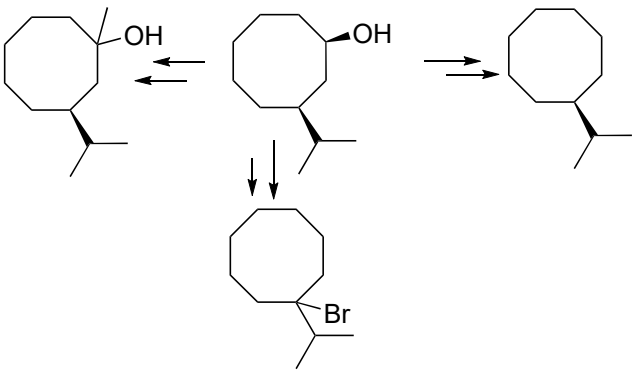
16) Proposer des conditions pour les réactions multi-étapes suivantes. Donner les mécanismes pour les étapes proposées.



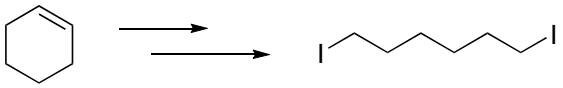
17) Donner les produits formés sous les conditions indiquées. Donner les mécanismes pour les étapes.



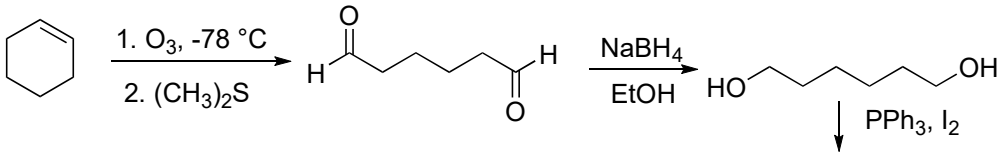
18) Proposer des conditions pour les réactions suivantes. Donner les mécanismes pour les étapes proposées.



1)

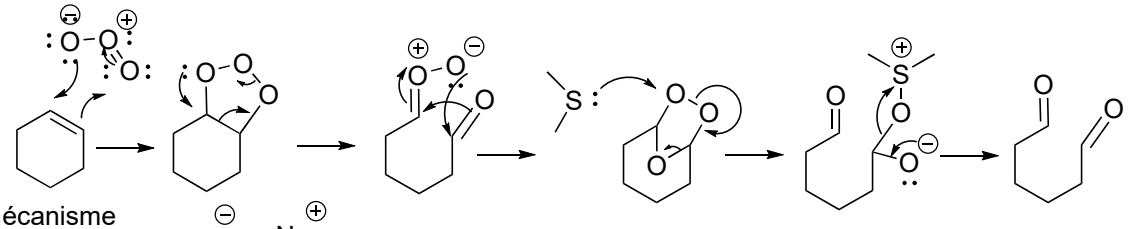


solution possible:

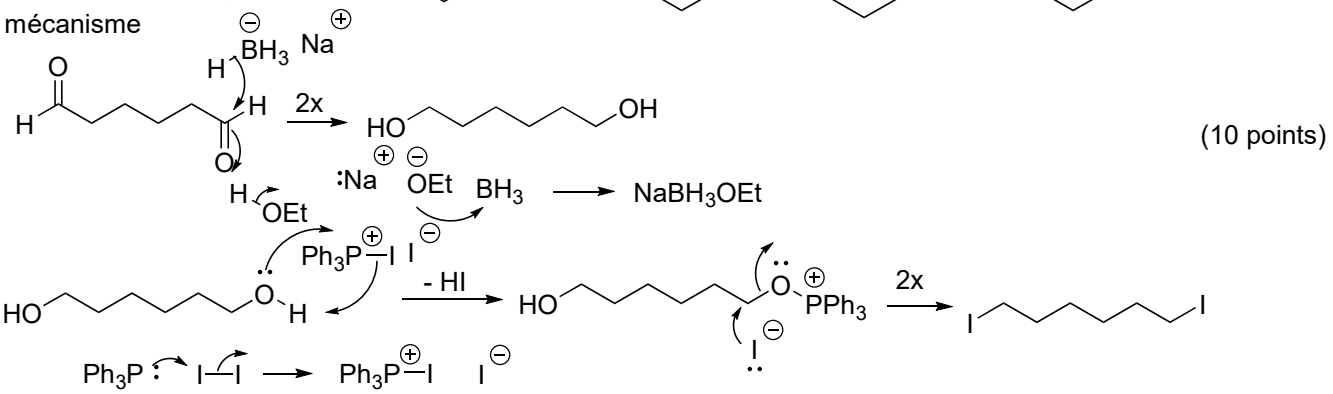


(3 points)

mécanisme



mécanisme



(10 points)

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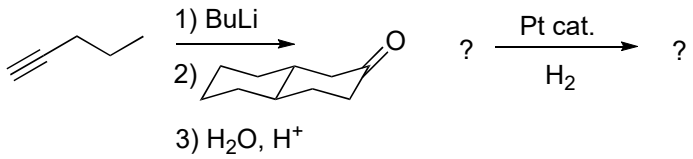
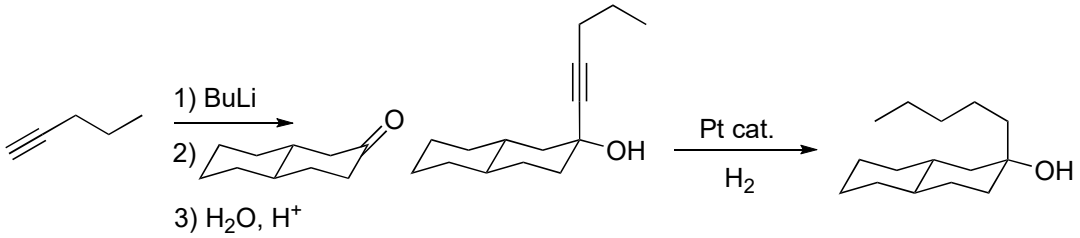
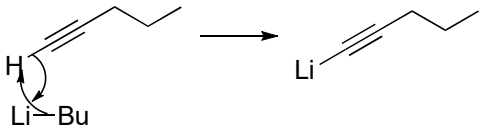
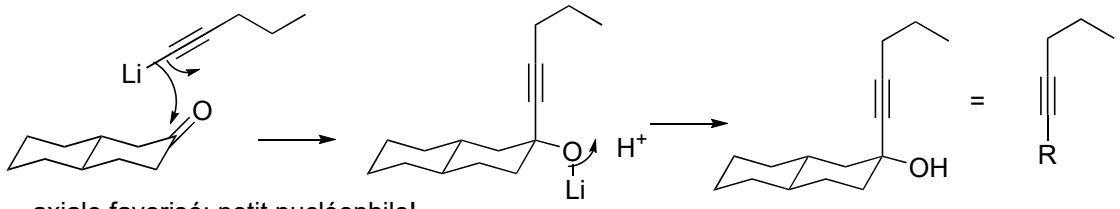




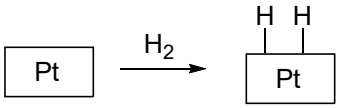
(2 points)

mécanisme

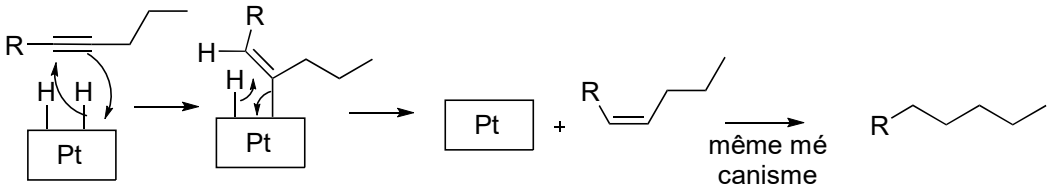




axiale favorisé: petit nucléophile!



(7 points)



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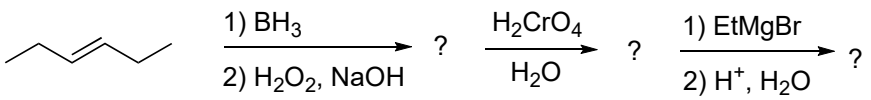
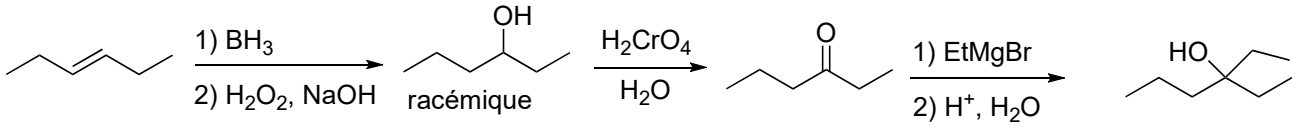
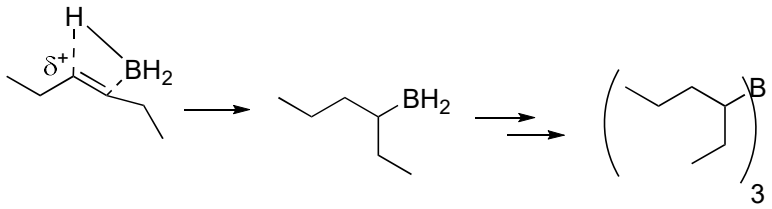
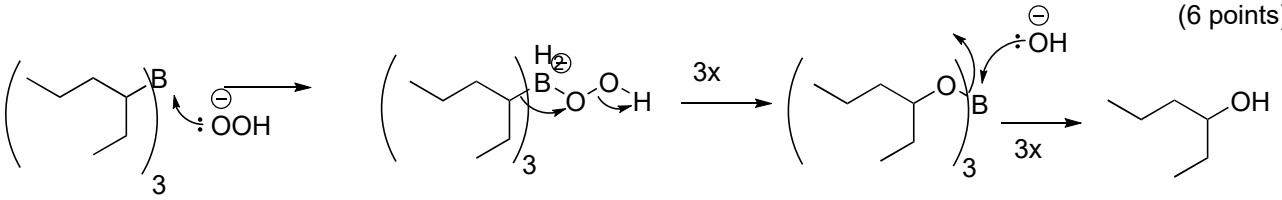




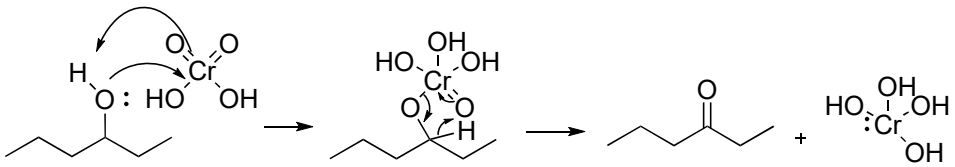
(3 points)



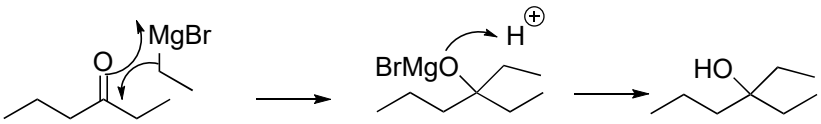
(6 points)



$NaOH + H_2O_2 \rightleftharpoons H_2O + NaOOH$

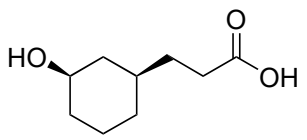


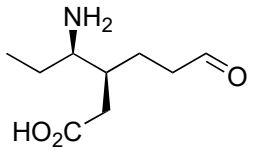
(2 points)

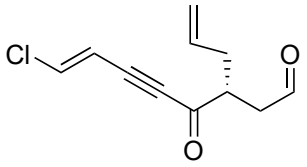


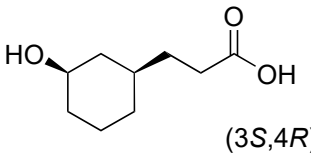
(2 points)

4) Donner le nom systématique IUPAC des molécules suivantes:



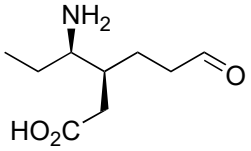




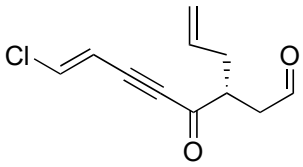


acide 3-((1*R*,3*R*)-3-hydroxycyclohexyl)propanoique (6 points)

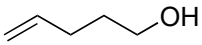
(3*S*,4*R*)-4-amino-3-(3-oxopropyl)hexanoic acid



acide (*S*)-3-((*R*)-1-aminopropyl)-6-oxo-hexanoique (6 points)



(*R*,*E*)-8-chloro-4-oxo-3-(prop-2-enyl)-oct-7-en-5-ynal (7 points)

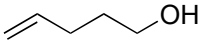
5) 

1) H_2CrO_4, H_2O
2) MeOH, H^+

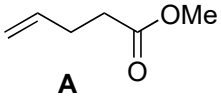
A

1) BH_3, THF
2) NaOH, H_2O_2
3) TBSCl, NEt_3, THF

B

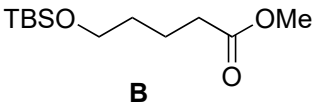


1) H_2CrO_4, H_2O
2) MeOH, H^+



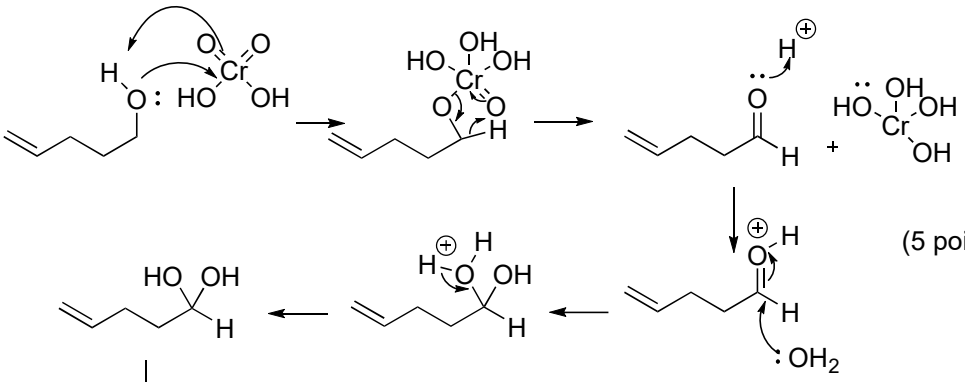
A

1) BH_3, THF
2) NaOH, H_2O_2
3) TBSCl, NEt_3, THF



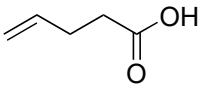
B

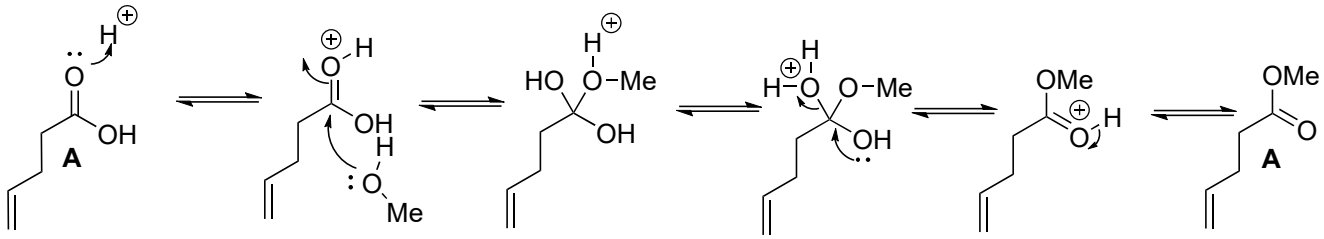
(2 points)



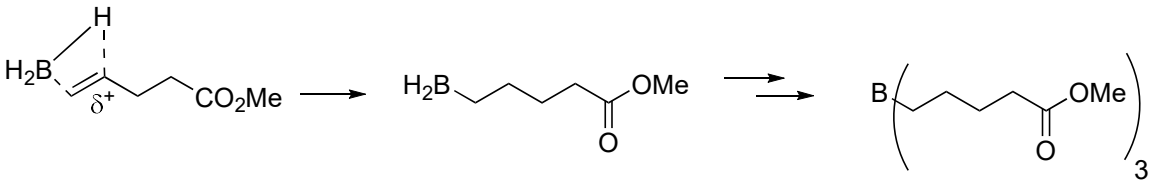
(5 points)

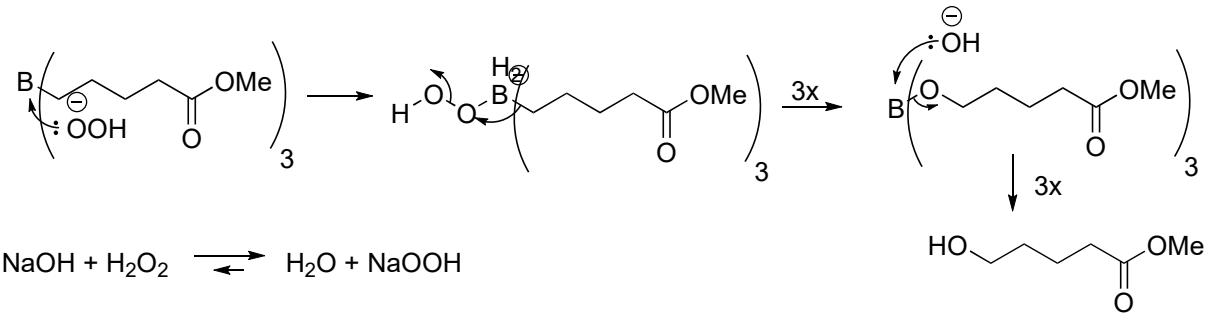
H_2CrO_4, même mécanisme





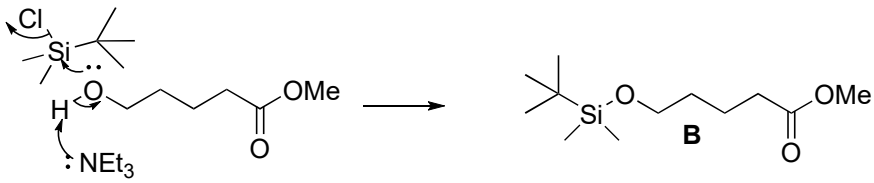
(5 points)





(6 points)

$NaOH + H_2O_2 \rightleftharpoons H_2O + NaOOH$

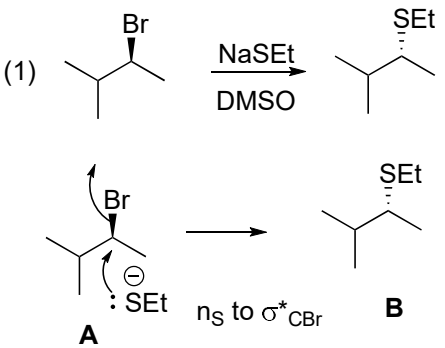


$+HNEt_3Cl$

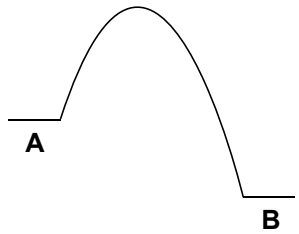
(1 point)

6)

(1)

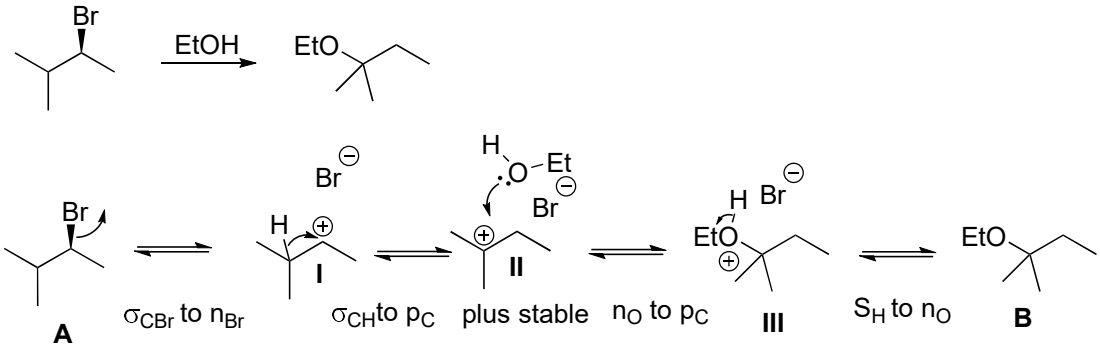


(2 points)



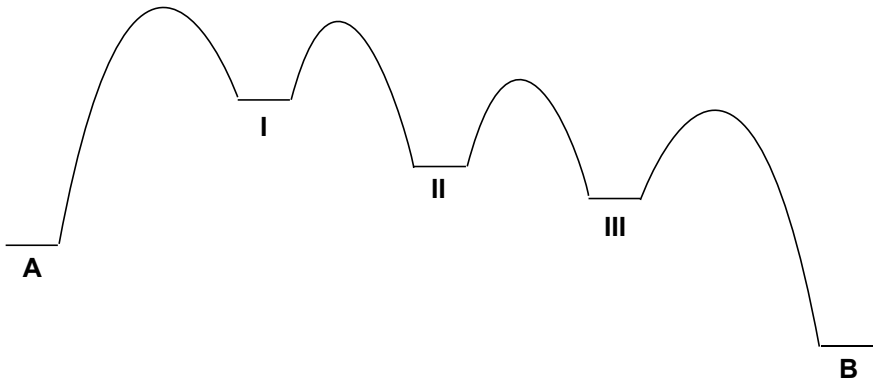
(1 points)

(2)



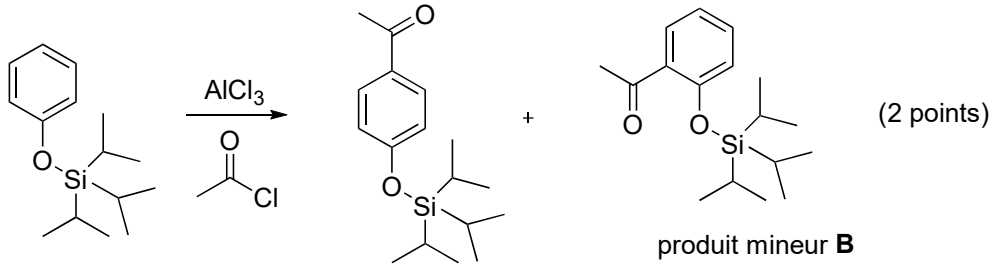
(4 points)

orbitales: 2 points

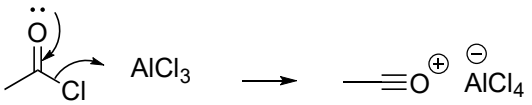


(3 points)

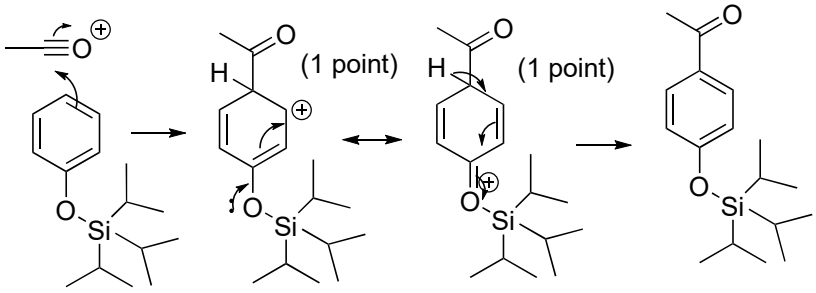
7)



(2 points)

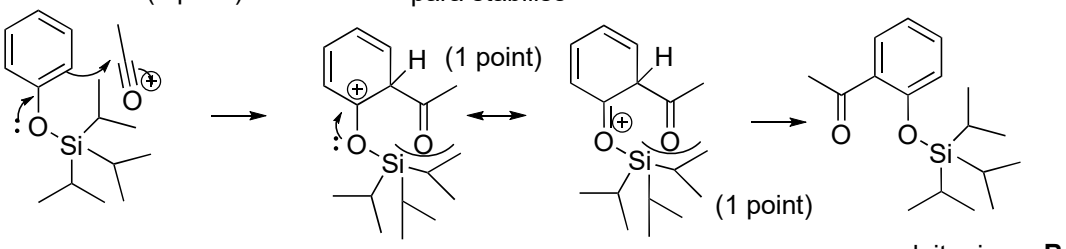


(1 point)



(1 point)

para stabilisé

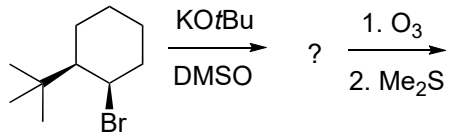


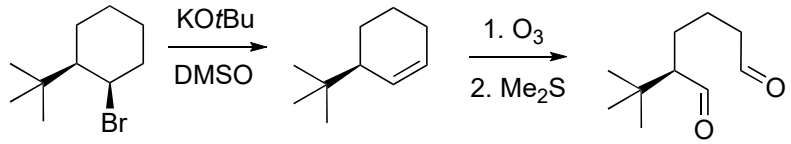
ortho stabilisé, mais stérique défavorable

meta pas stabilisé

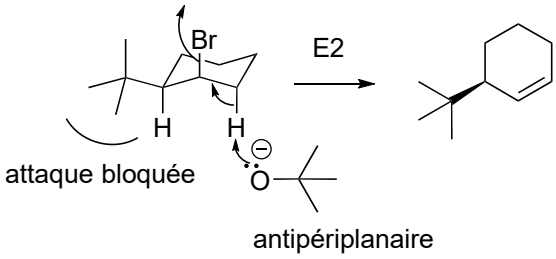
(total: 6 points)

8)

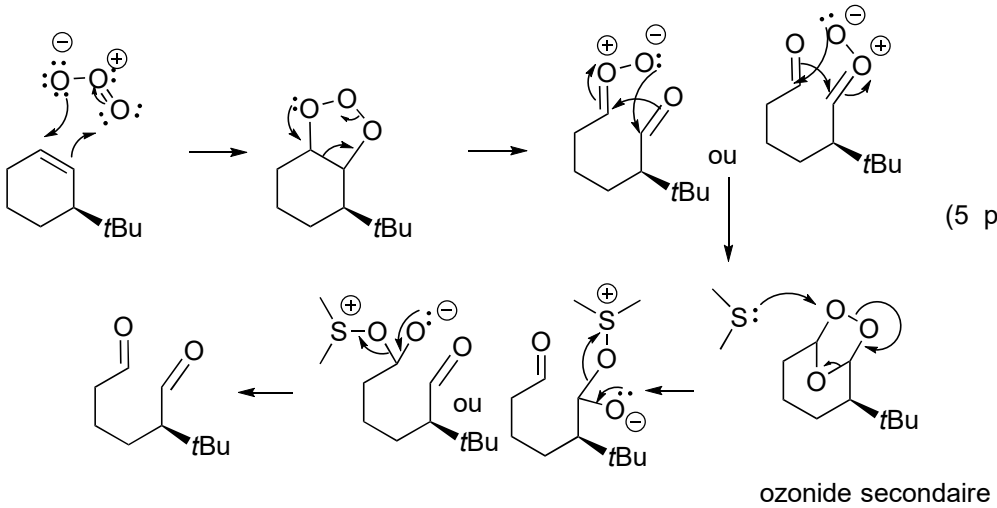




(2 points)



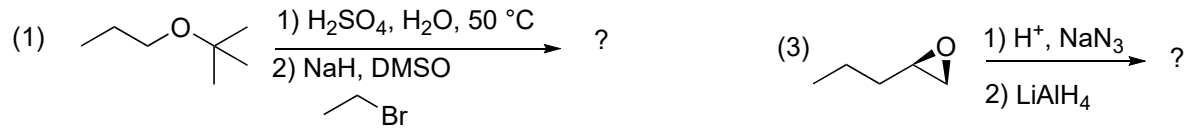
(2 points)



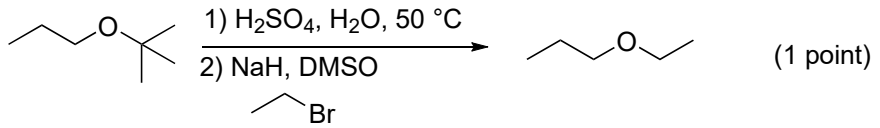
(5 points)

9)

Donner les produits et les mécanismes des réactions suivantes.

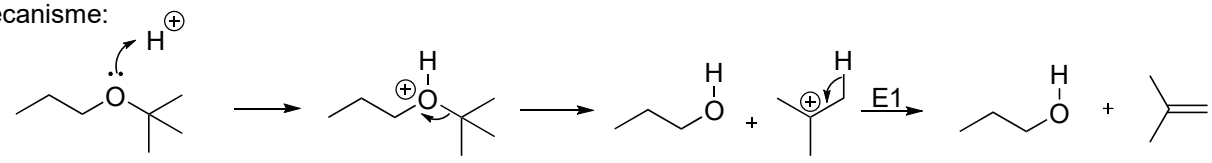


(1)



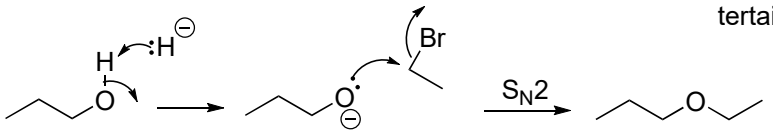
(1 point)

mécanisme:



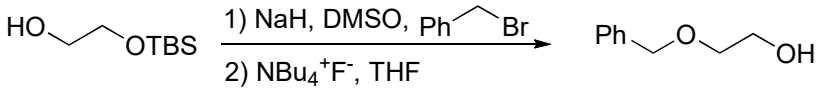
carbocation tertaire favorisé

(3 points)



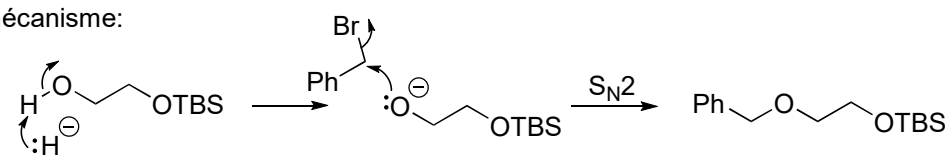
(2 points)

(2)

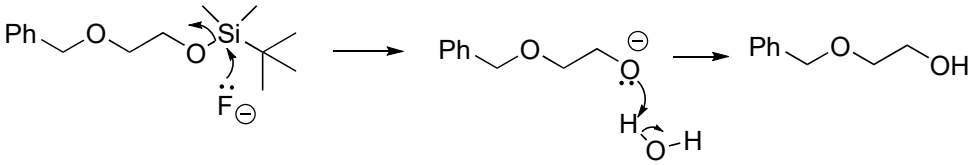


(1 point)

mécanisme:

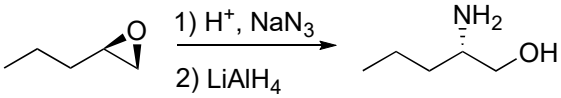


(2 points)



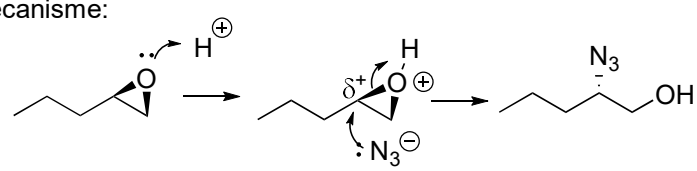
(2 points)

(3)



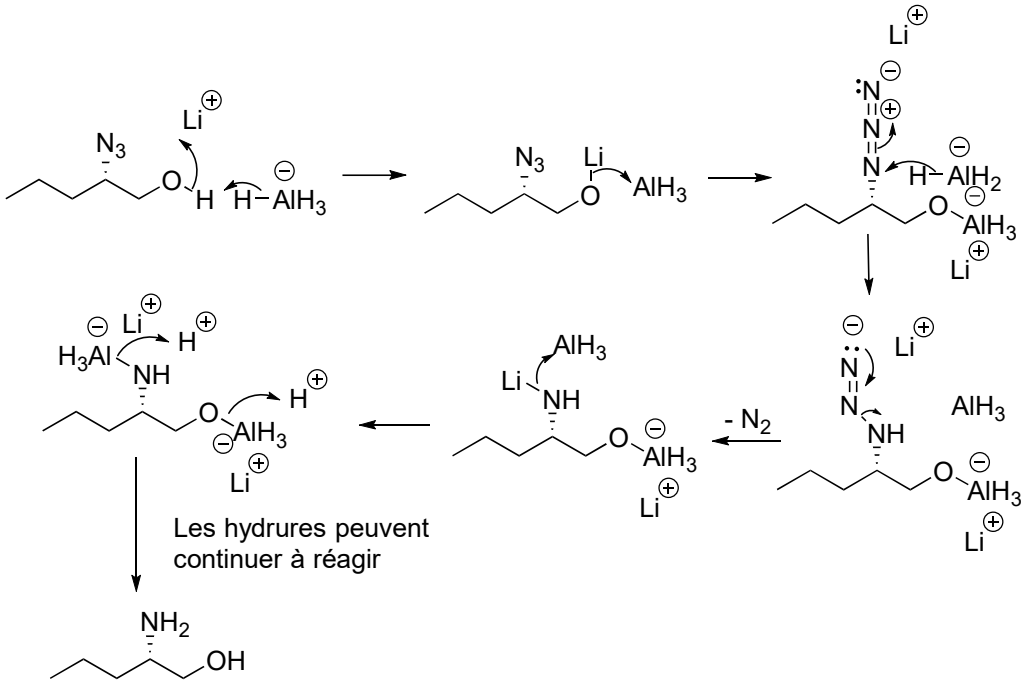
(1 point)

mécanisme:



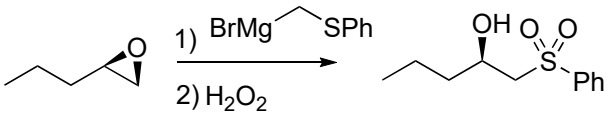
(2 points)

charge partielle positive stabilisé
e en position secondaire

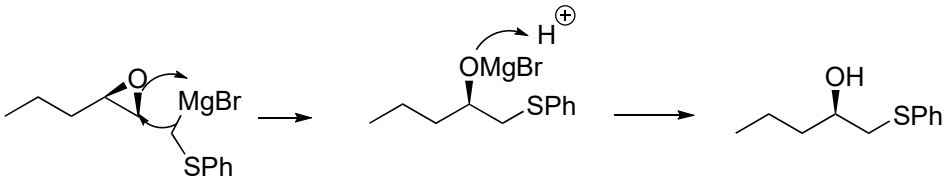


(5 points)

(4)

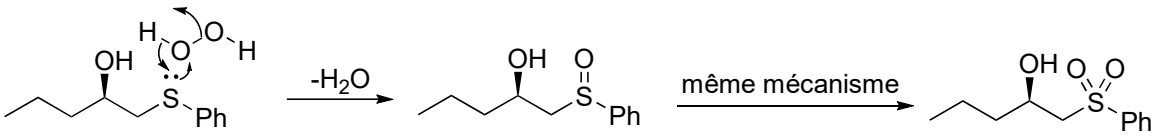


(1 point)



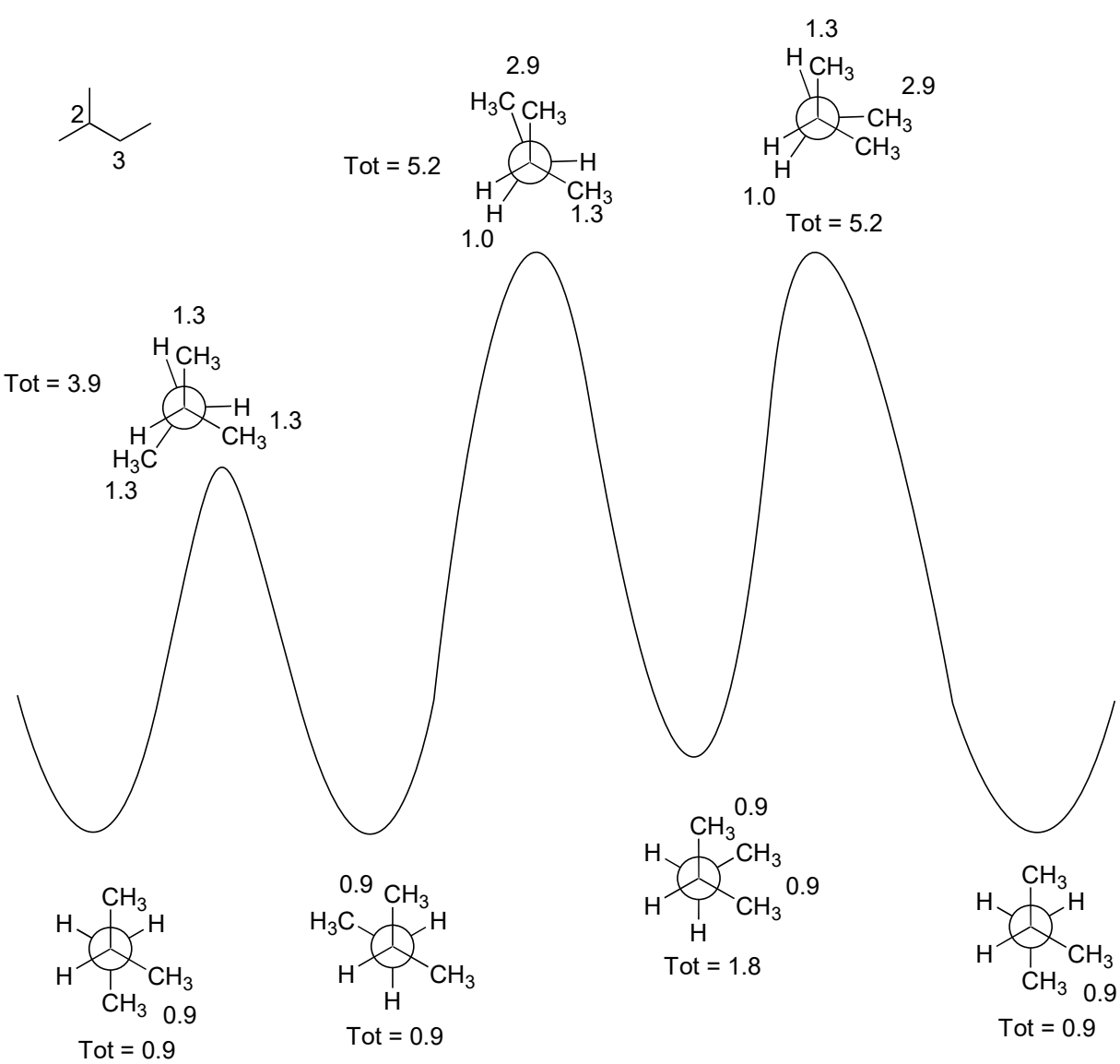
(2 points)

position moins substituée



(2 points)

10)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3
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1.3
H
CH3
H
1.3
CH3
H
H3C
1.3
Tot = 5.2
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CH3
H
CH3
1.3
H
H
1.0
1.3
H
CH3
2.9
CH3
H
CH3
H
1.0
Tot = 5.2
CH3
H
H
H
CH3
CH3
0.9
Tot = 0.9
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CH3
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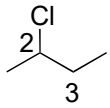
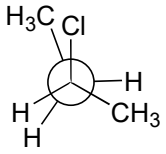
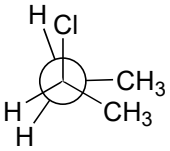
CH3
0.9
Tot = 0.9



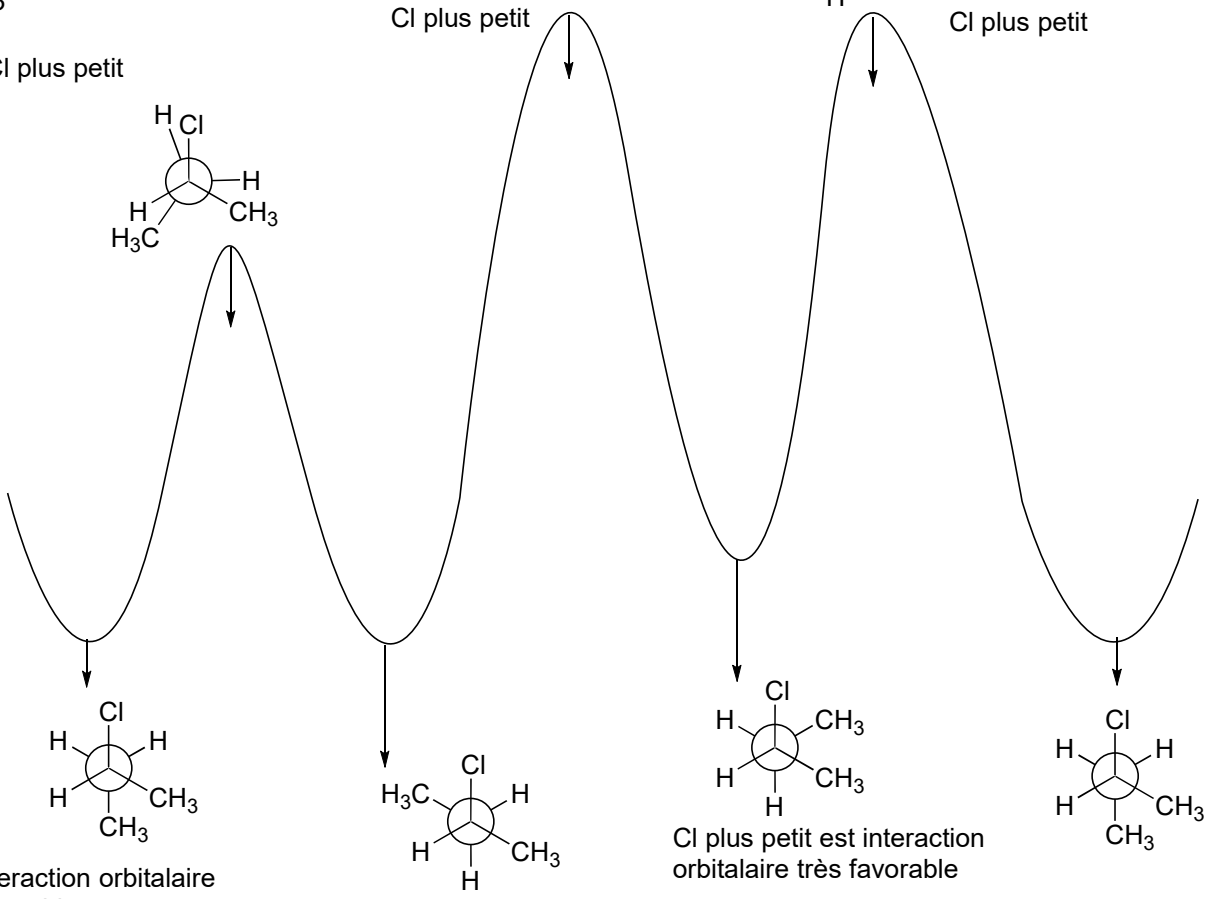
Cl plus petit



Cl plus petit



Cl plus petit

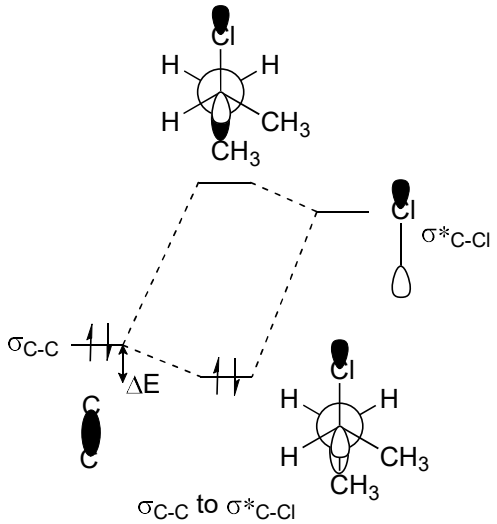


interaction orbitalaire favorable

Cl plus petit est interaction orbitalaire très favorable

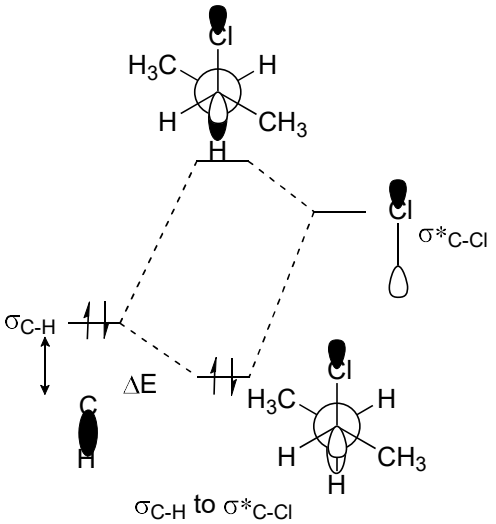
Cl plus petit est interaction orbitalaire très favorable

interactions orbitalaires favorables supplémentaires pour Cl:



σ_{C-C} to σ^*_{C-Cl}

E = 2ΔE

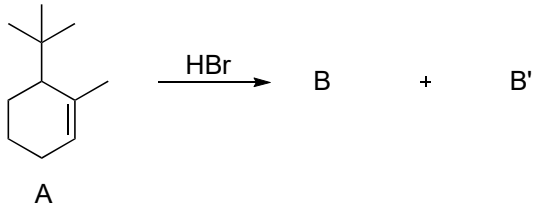


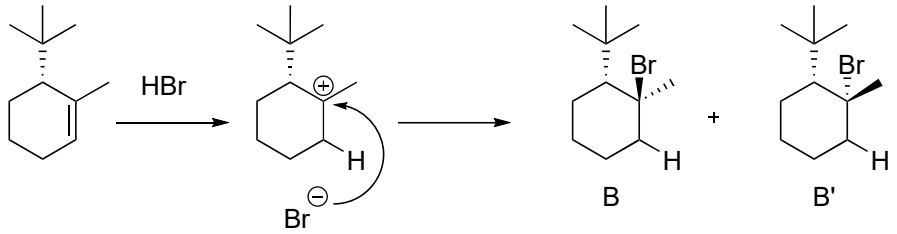
σ_{C-H} to σ^*_{C-Cl}

E = 2ΔE

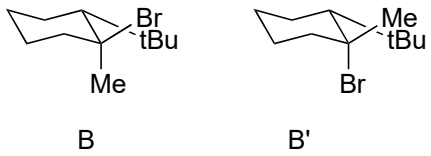
légèrement meilleur (H plus électropositif que C)

11)



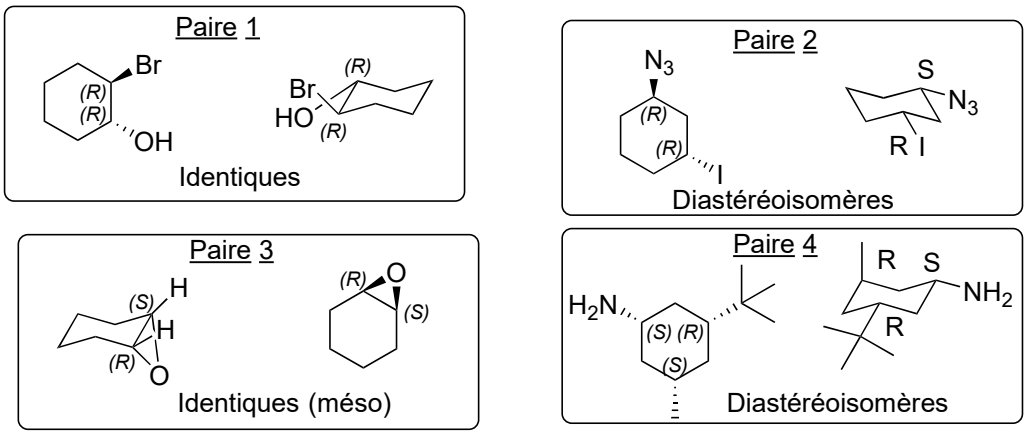


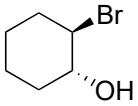
Formation du carbocation le plus stable B et B' sont diastéréoisomères



Le produit B’ est le plus stable. En effet, le groupe méthyl se trouve en position équatorial, ce qui sera favorisé.

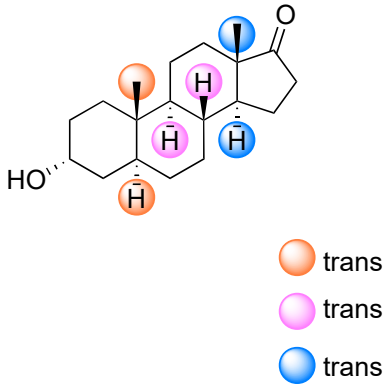
12)

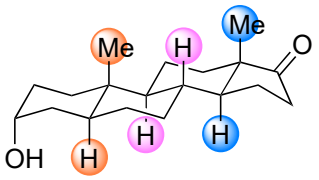




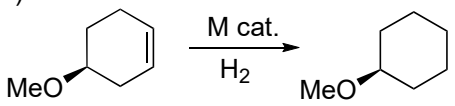
(1*R*,2*R*)-2-bromocyclohexan-1-ol

13)

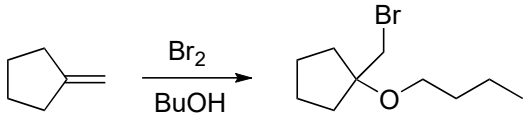




14)

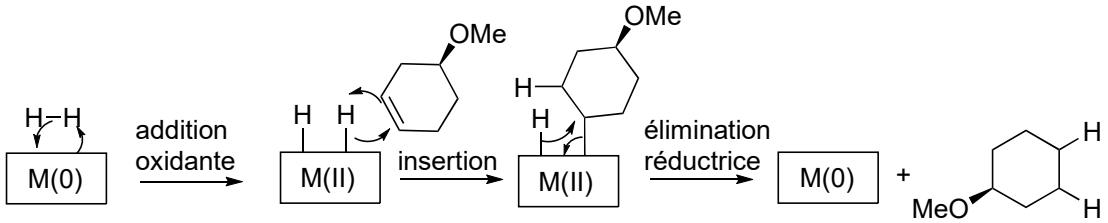


M = Pd, Pt, Ni or Rh

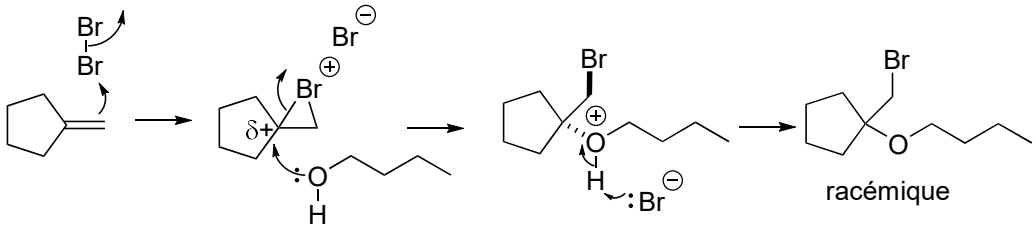


racémique

(2 points)



(3 points)

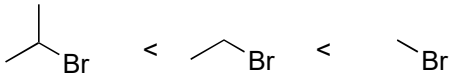


racémique

(4 points)

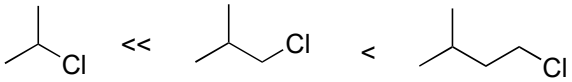
charge partielle en tertiaire
Attaque opposée à Br

15)

a) 

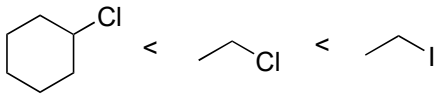
(2 points)

effet stérique sur l'état de transition: les substituants ralentissent la réaction

b) 

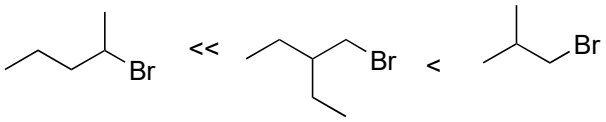
(2 points)

L'effet stérique diminue de secondaire à primaire et avec l'éloignement des substituants

c) 

(2 points)

1) effet stérique: secondaire plus lent que primaire
2) L'iode est un meilleur groupe partant (électrons stabilisés sur grand atome)

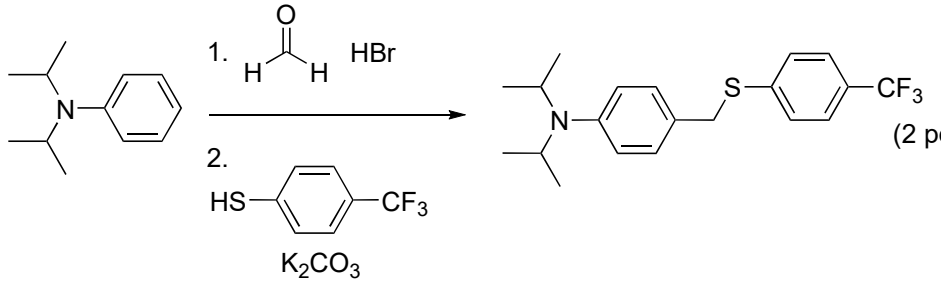
d) 

(2 points)

Effet stérique: secondaire à primaire et ethyl plus grand que méthyl

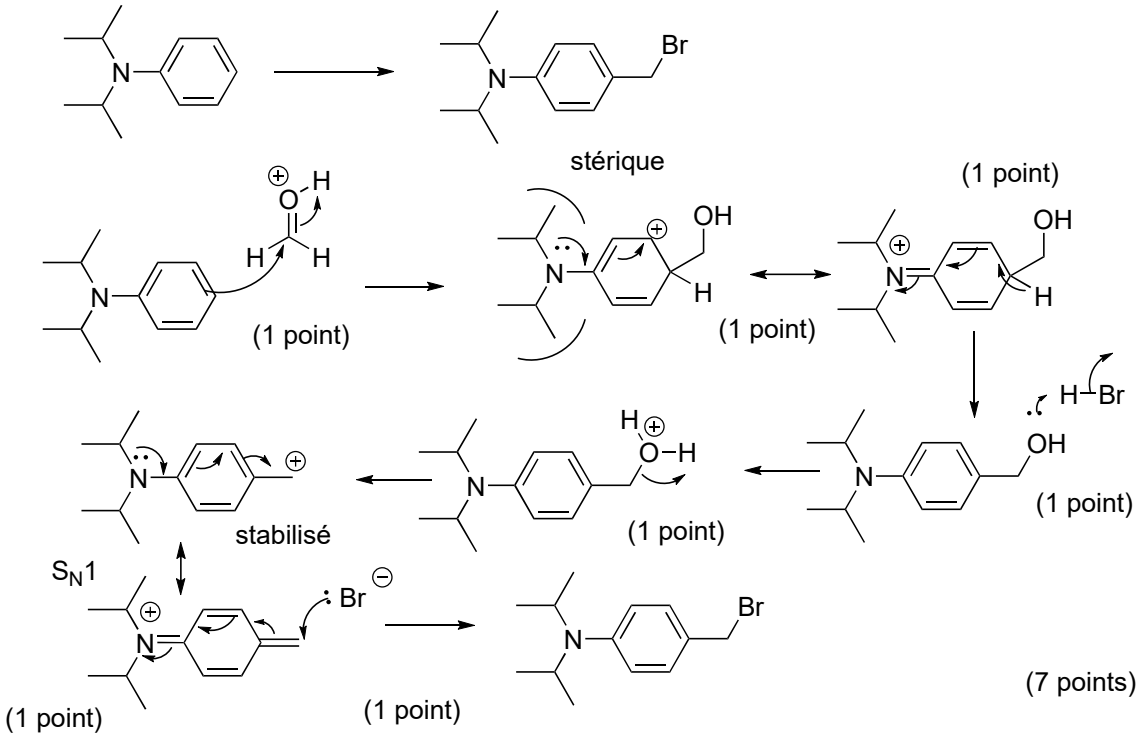
16)

(1)

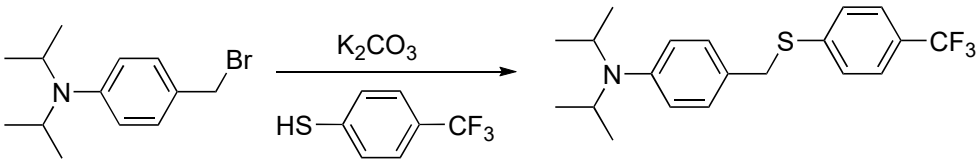


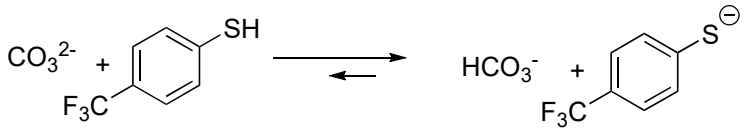
(2 points)

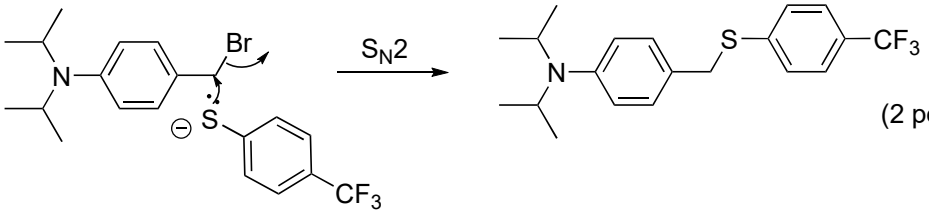
mécanisme



(7 points)

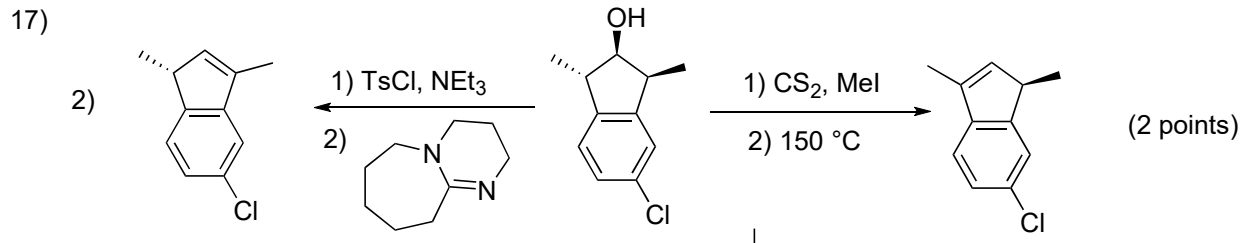






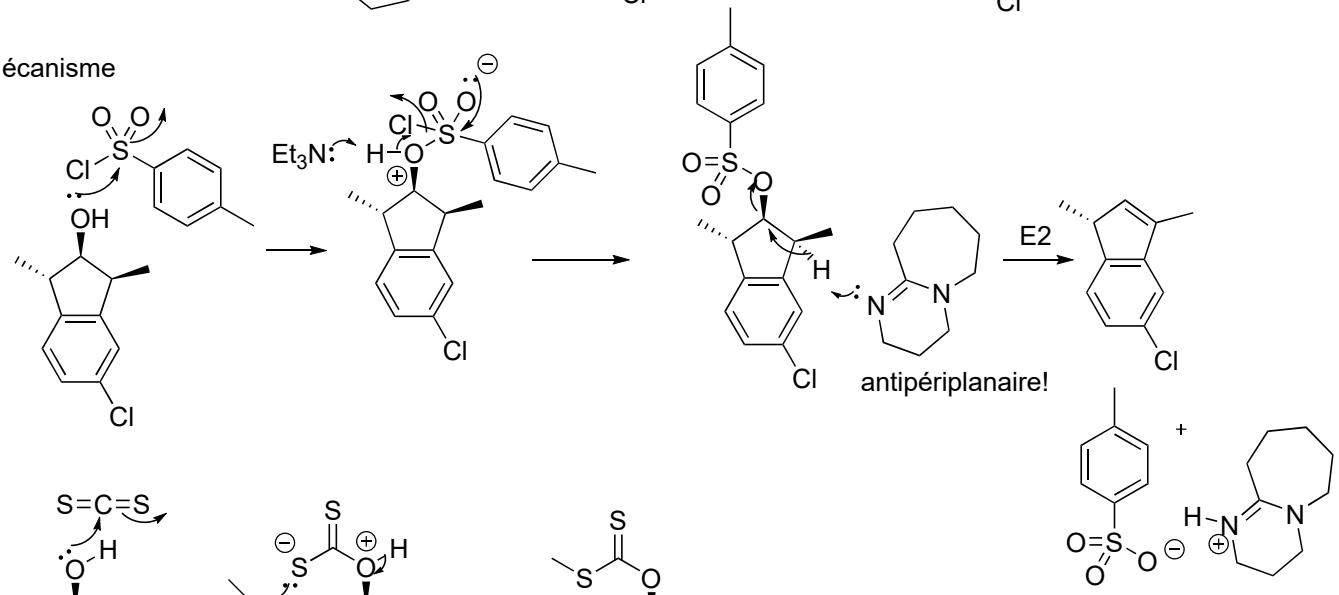
(2 points)

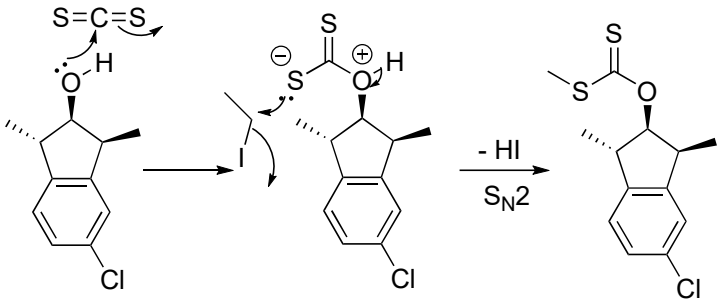
17)



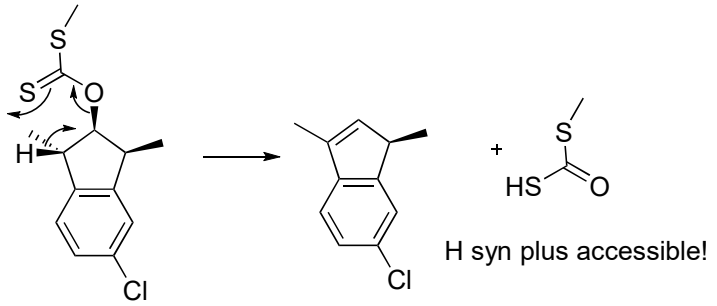
(2 points)

mécanisme





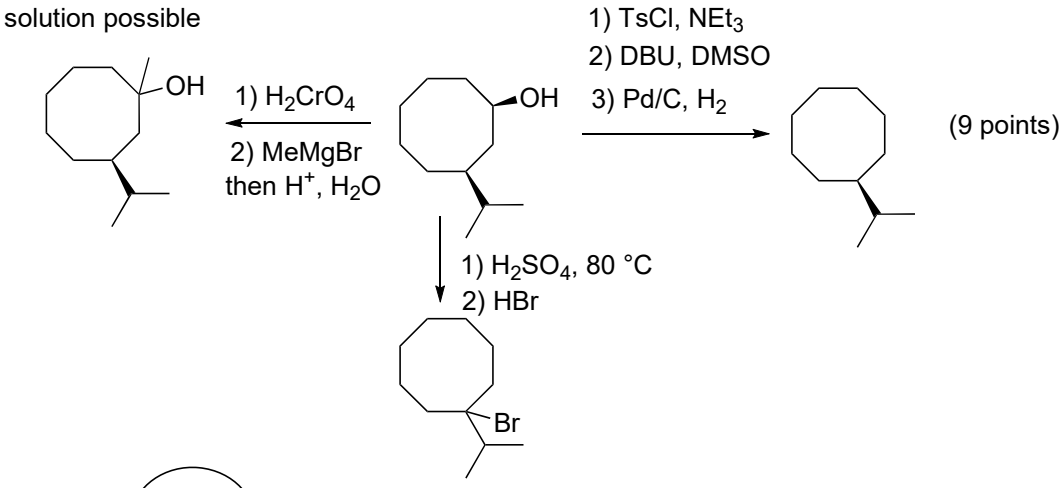
(6 points)



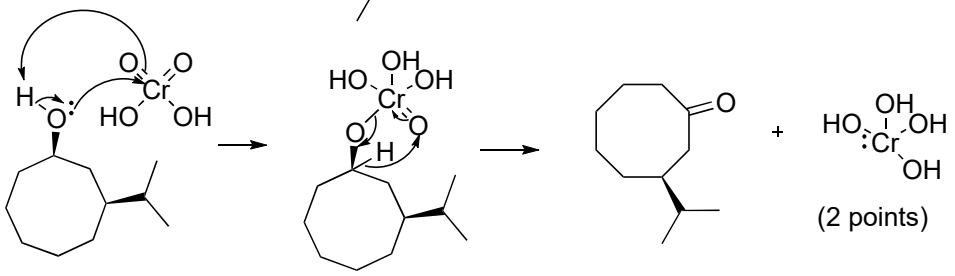
H syn plus accessible!

18)

solution possible



(9 points)



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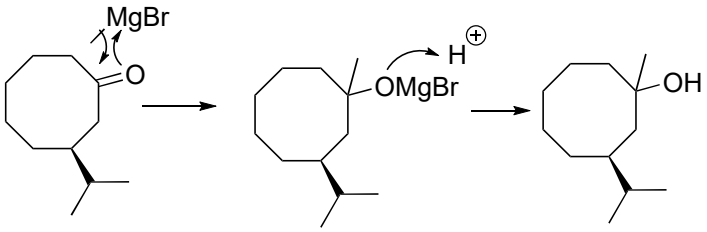

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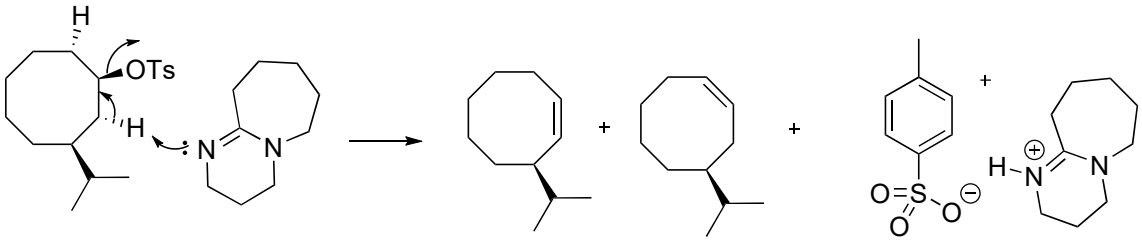
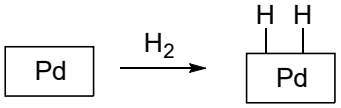
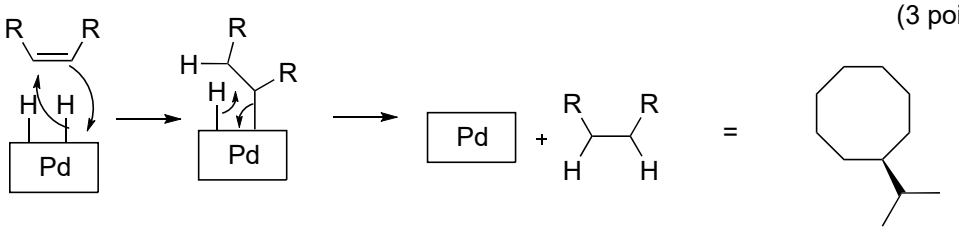


mélange, 2 H accessible

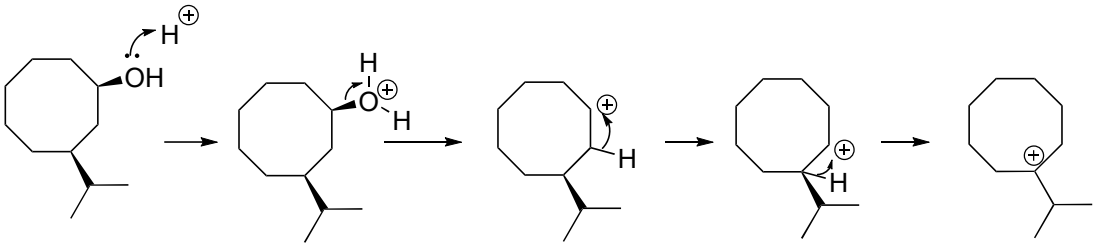
(1 point)



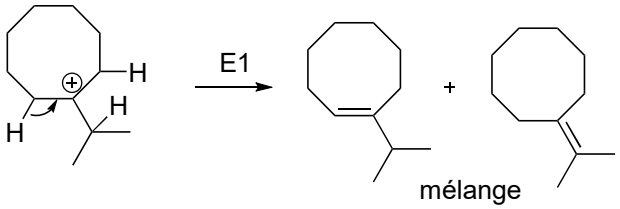
(3 points)



même produit obtenu

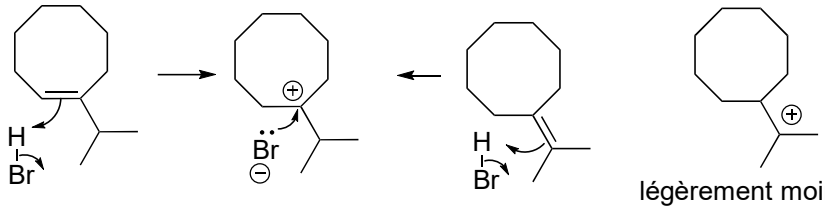


tertiaire: plus stable



mélange

(4 points)



(2 points)

légèrement moins stable, mais probablement quand même formé: produit minoritaire