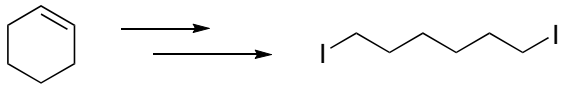
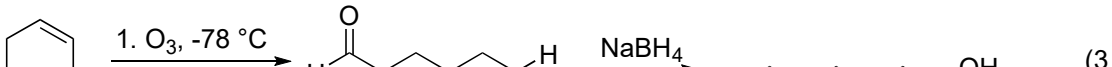
1)

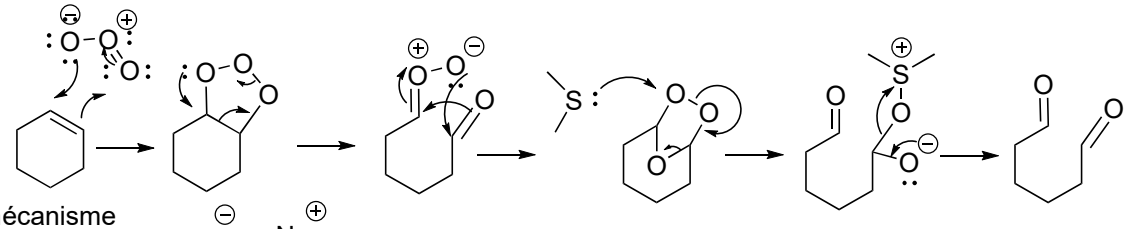


solution possible:

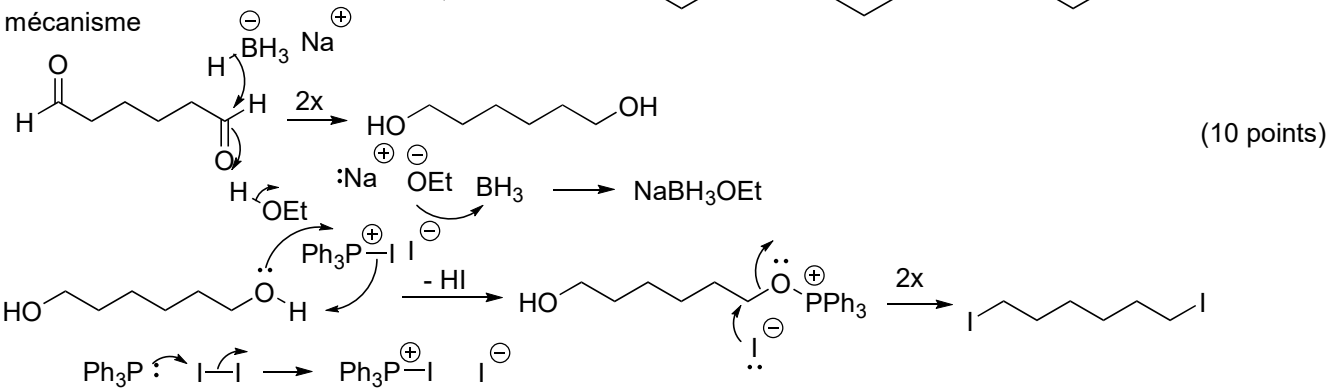


(3 points)

mécanisme

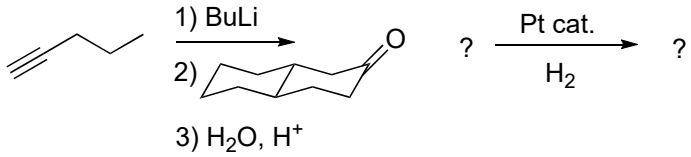


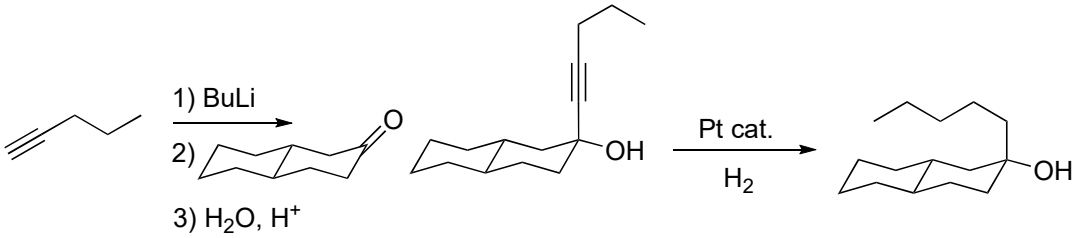
mécanisme



(10 points)

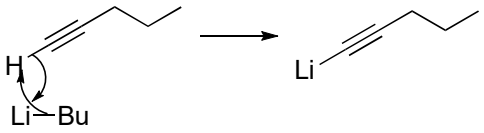
2)

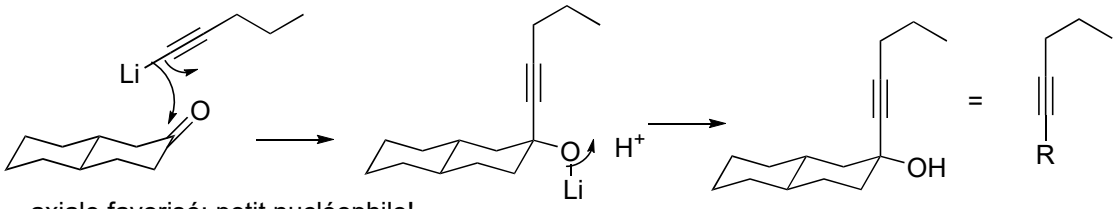




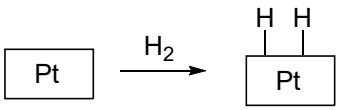
(2 points)

mécanisme

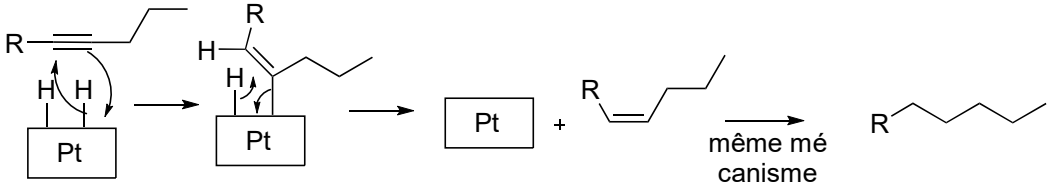




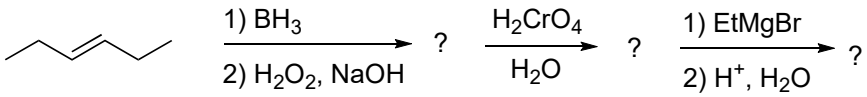
axiale favorisé: petit nucléophile!

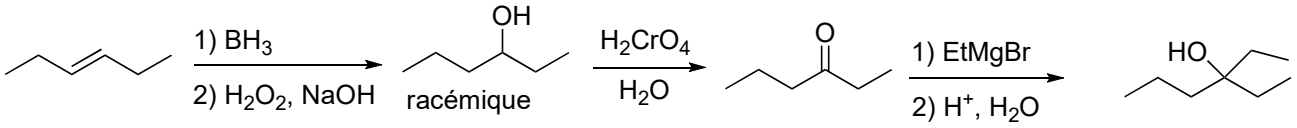


(7 points)

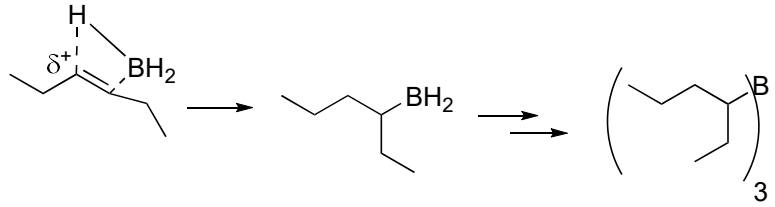


3)

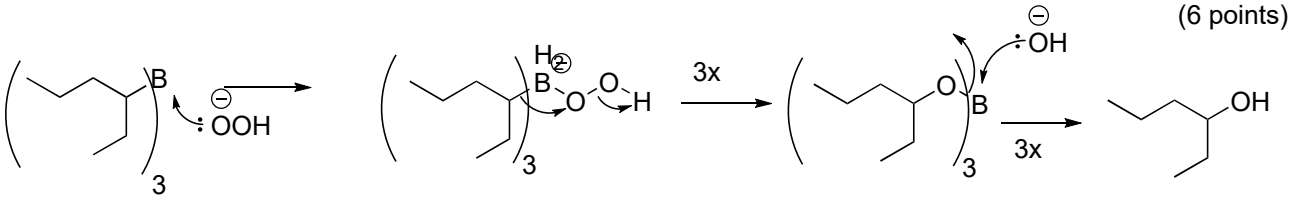




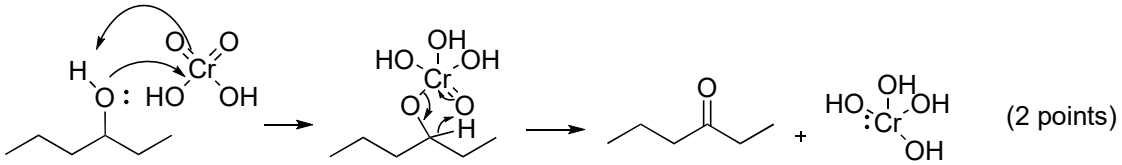
(3 points)



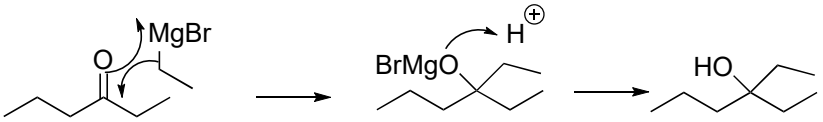
(6 points)



$NaOH + H_2O_2 \rightleftharpoons H_2O + NaOOH$

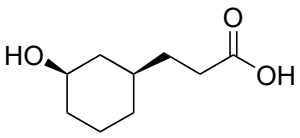


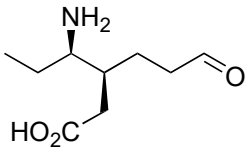
(2 points)

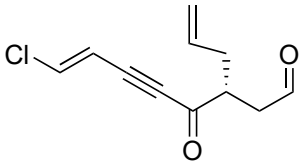


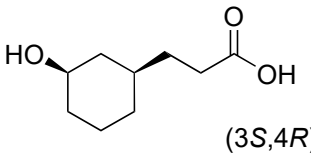
(2 points)

4) Donner le nom systématique IUPAC des molécules suivantes:



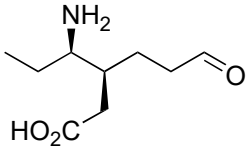




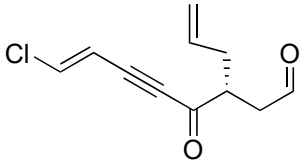


acide 3-((1*R*,3*R*)-3-hydroxycyclohexyl)propanoique (6 points)

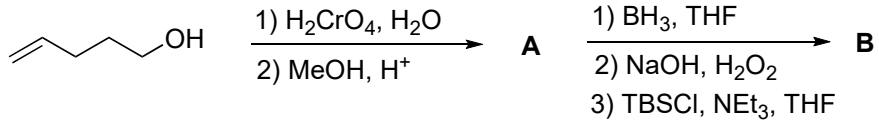
(3*S*,4*R*)-4-amino-3-(3-oxopropyl)hexanoic acid

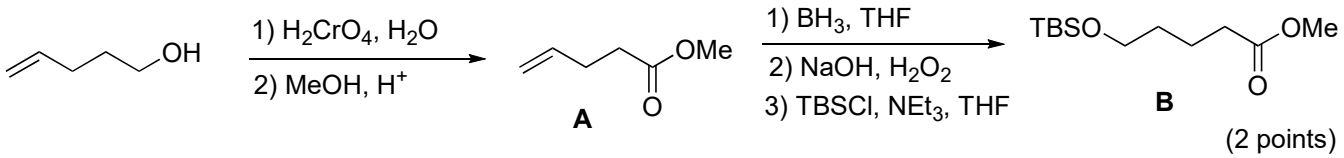


acide (*S*)-3-((*R*)-1-aminopropyl)-6-oxo-hexanoique (6 points)

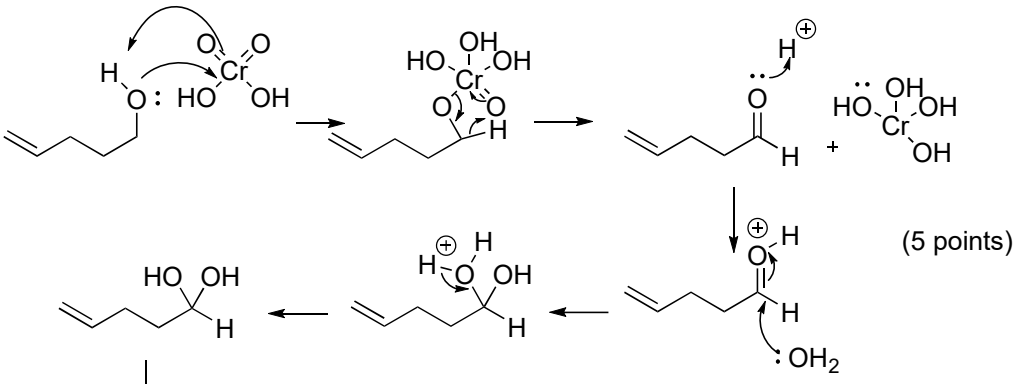


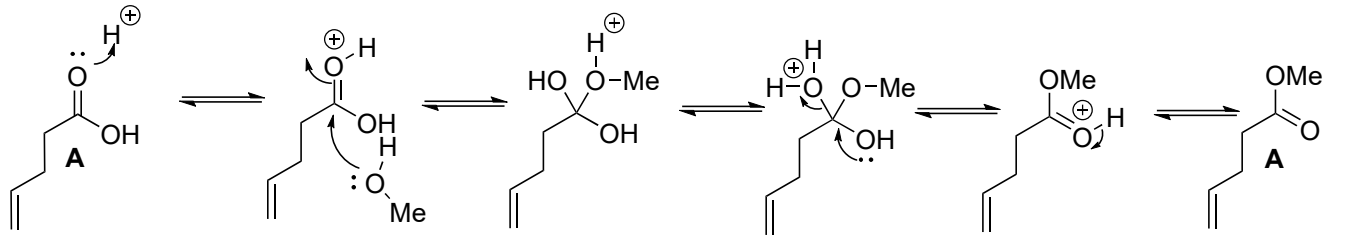
(*R*,*E*)-8-chloro-4-oxo-3-(prop-2-enyl)-oct-7-en-5-ynal (7 points)

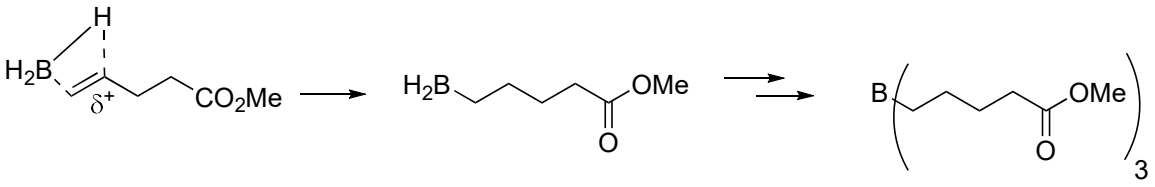
5) 
OH
1) H_2CrO_4, H_2O
2) MeOH, H^+
A
1) BH_3, THF
2) NaOH, H_2O_2
3) TBSCl, NEt_3, THF
B

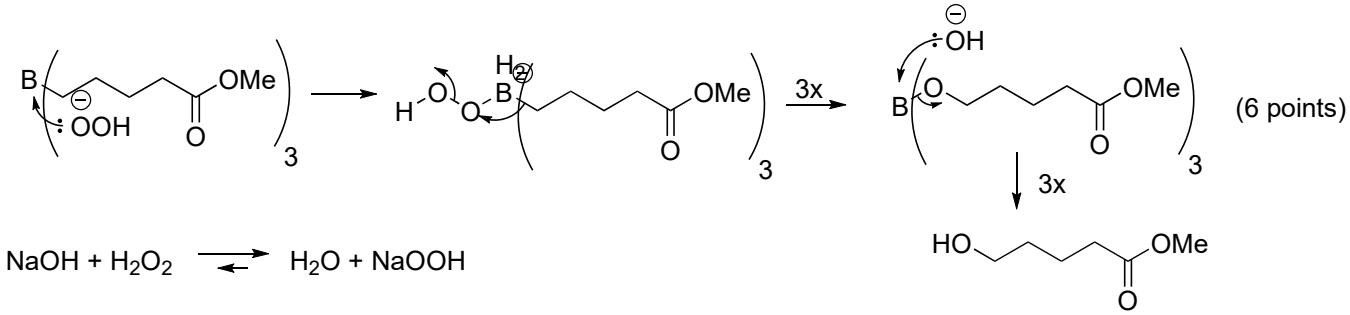

OH
1) H_2CrO_4, H_2O
2) MeOH, H^+
OMe
A
1) BH_3, THF
2) NaOH, H_2O_2
3) TBSCl, NEt_3, THF
TBSO
OMe
B

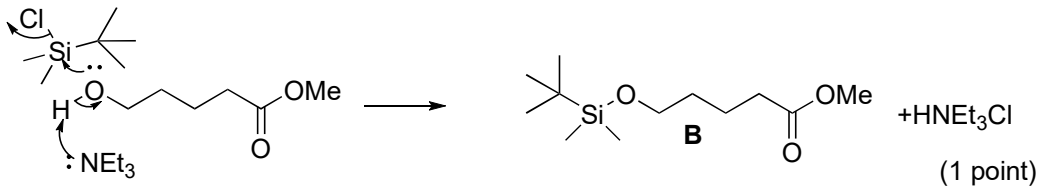
(2 points)


(5 points)
H_2CrO_4, même mécanisme


A
A
(5 points)

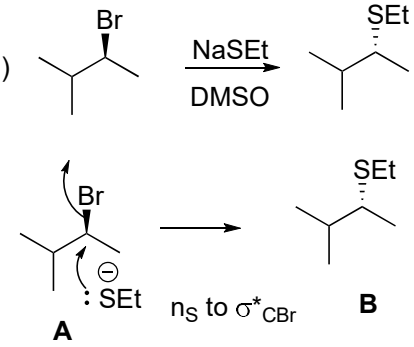



3x
3x
(6 points)
$NaOH + H_2O_2$ $H_2O + NaOOH$

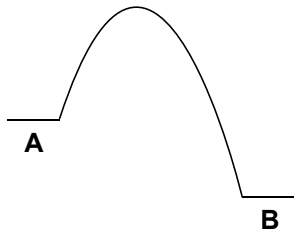

B
$+HNEt_3Cl$
(1 point)

6)

(1)

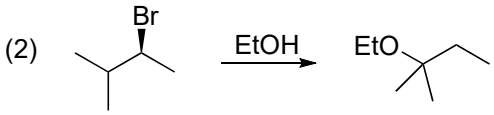


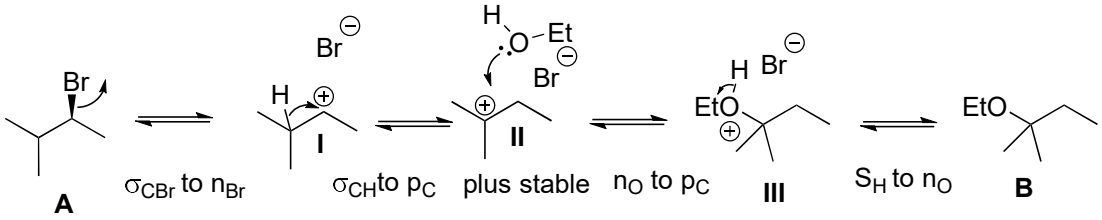
(2 points)



(1 points)

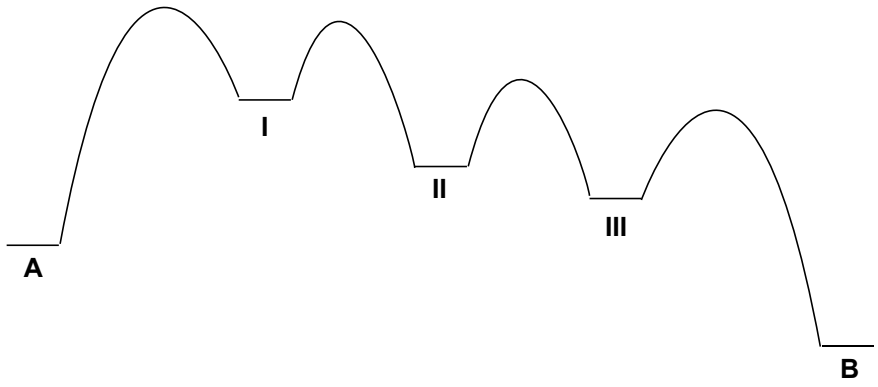
(2)





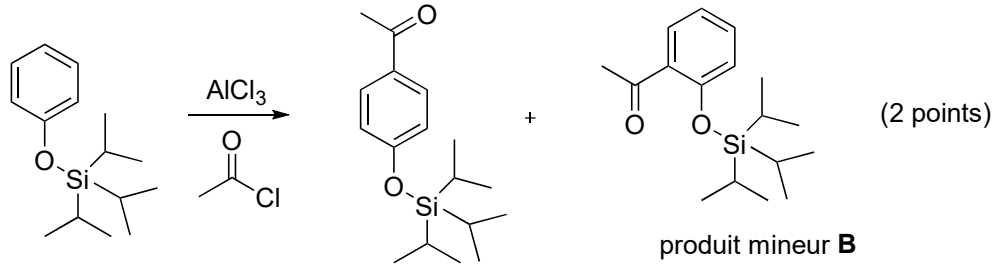
(4 points)

orbitales: 2 points



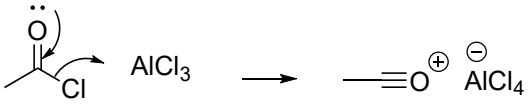
(3 points)

7)

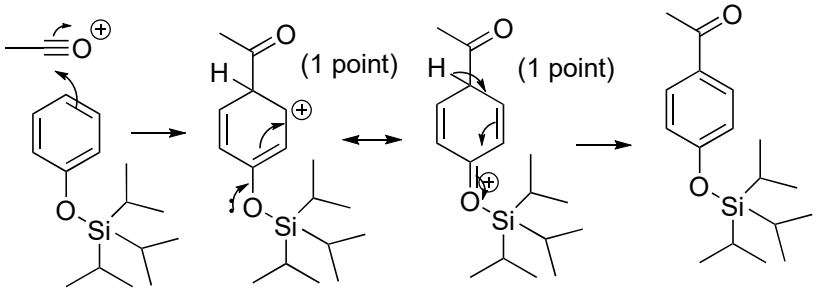


(2 points)

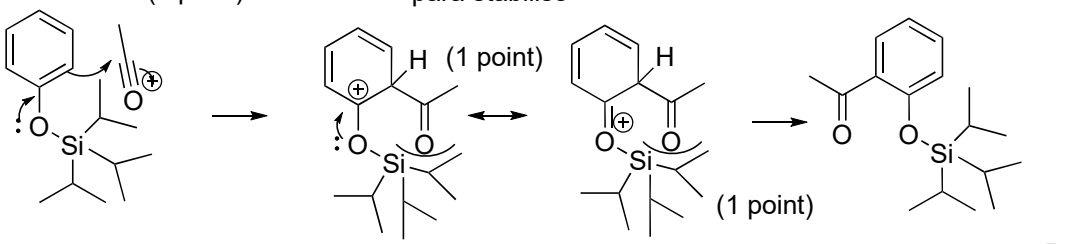
produit mineur **B**



(1 point)



(1 point) para stabilisé produit majeur **A**



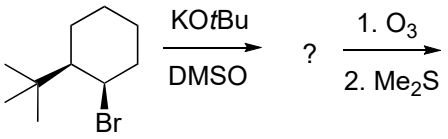
(1 point)

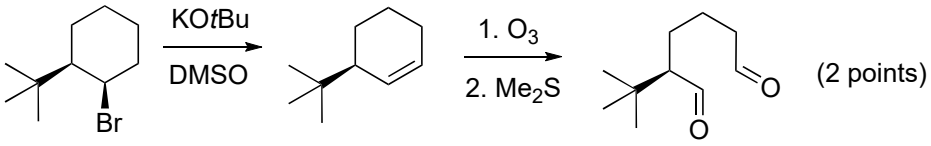
ortho stabilisé, mais stérique défavorable produit mineur **B**

meta pas stabilisé

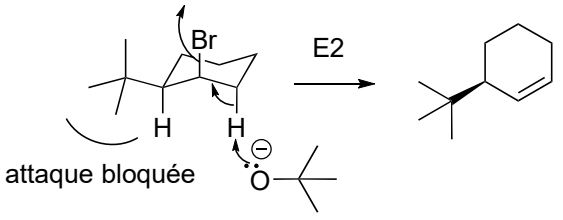
(total: 6 points)

8)

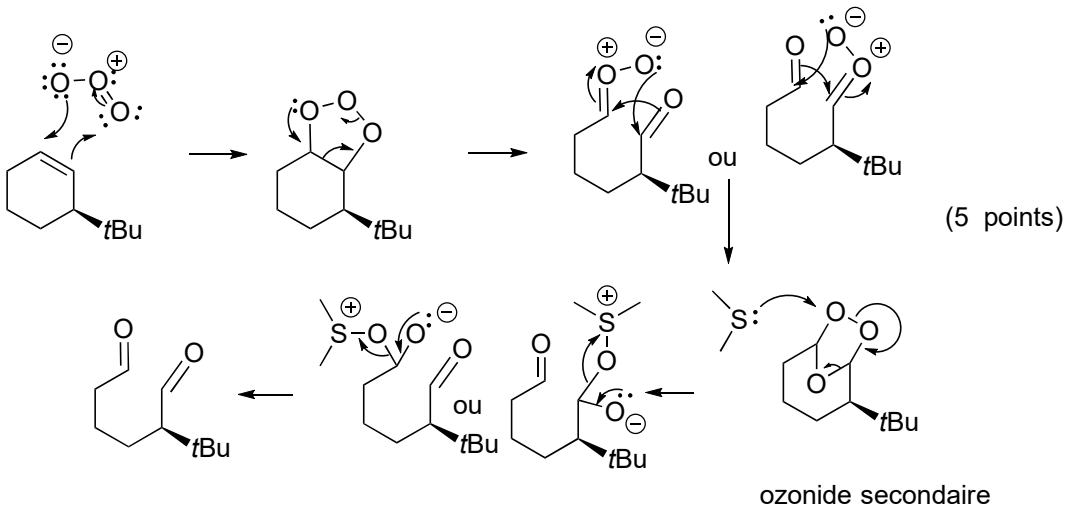




(2 points)



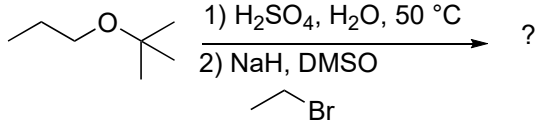
(2 points)

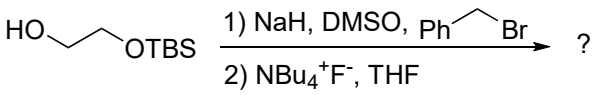


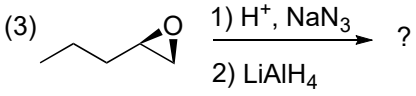
(5 points)

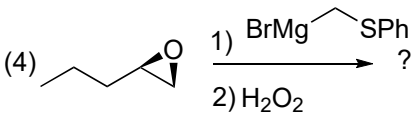
9)

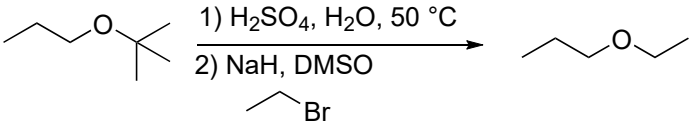
Donner les produits et les mécanismes des réactions suivantes.

(1) 

(2) 

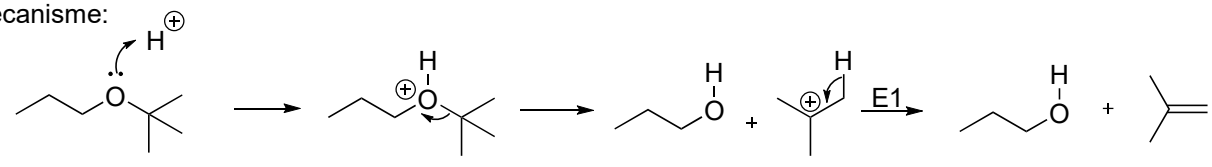
(3) 

(4) 

(1) 

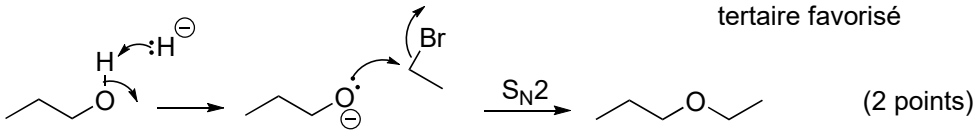
(1 point)

mécanisme:

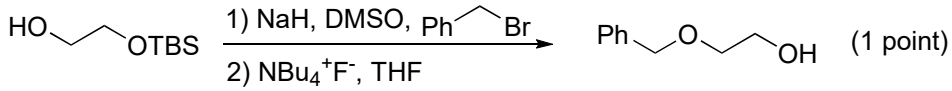


carbocation tertiaire favorisé

(3 points)

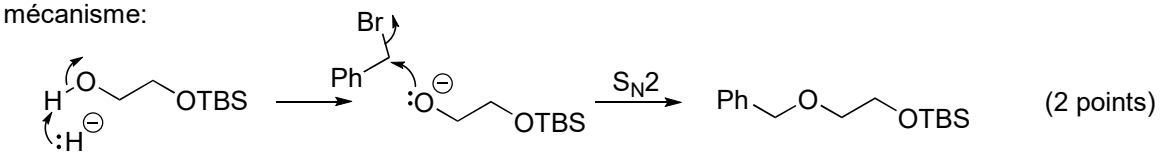


(2 points)

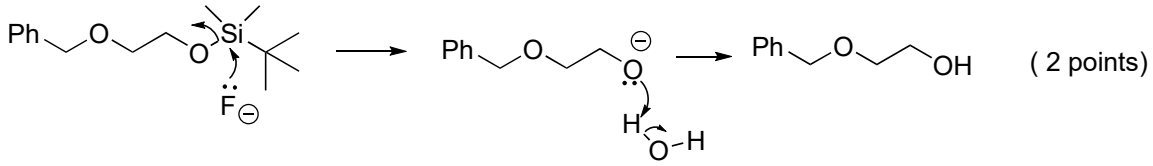
(2) 

(1 point)

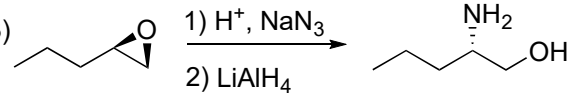
mécanisme:



(2 points)

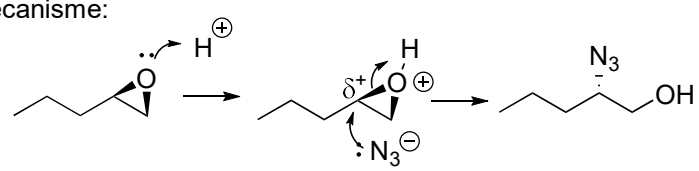


(2 points)

(3) 

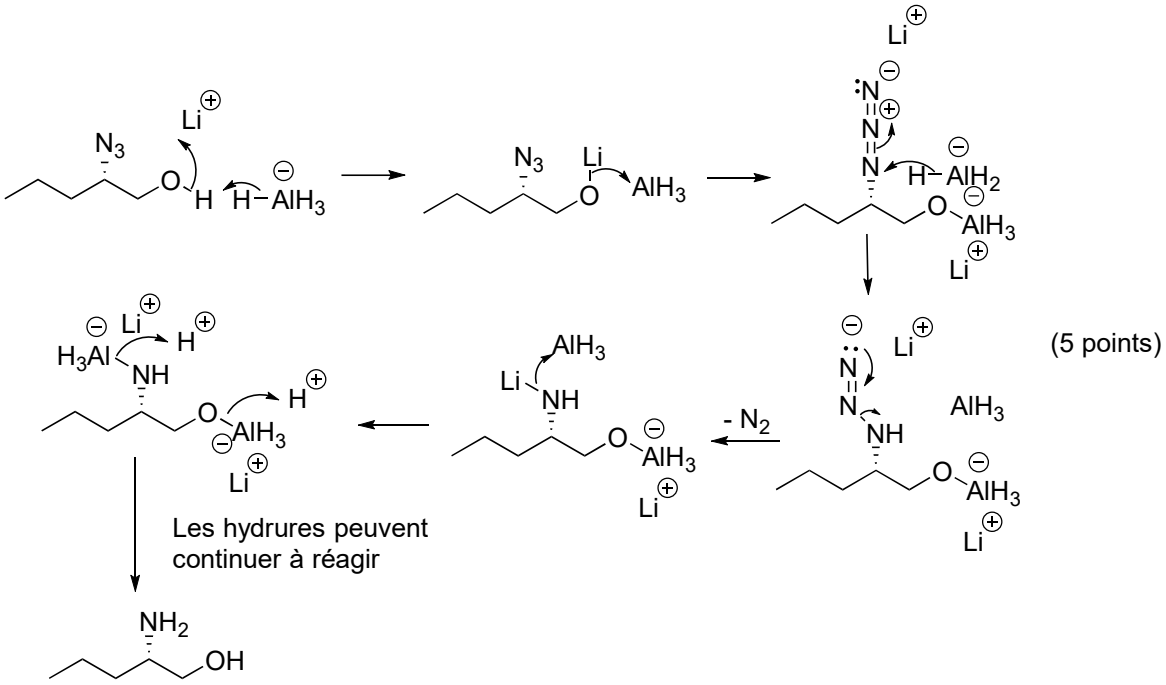
(1 point)

mécanisme:



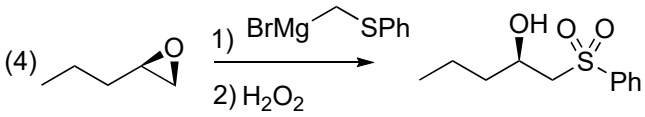
(2 points)

charge partielle positive stabilisé
e en position secondaire

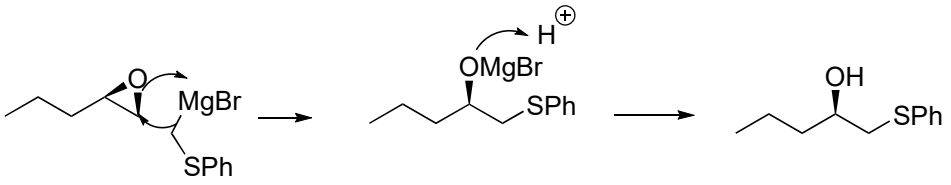


(5 points)

(4)

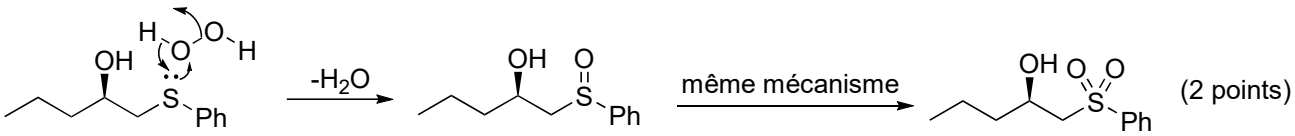


(1 point)



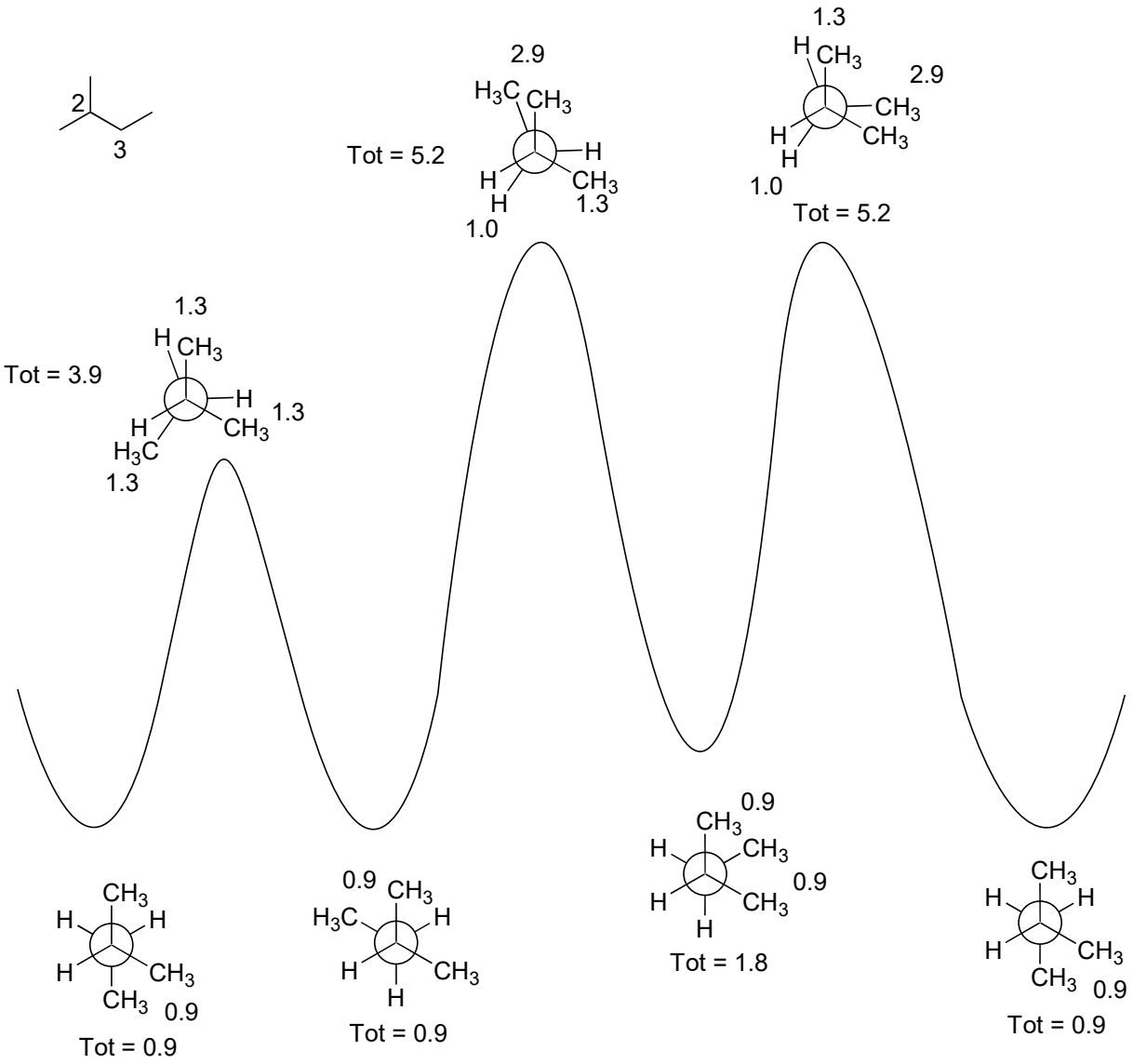
(2 points)

position moins substituée



(2 points)

10)


2
3
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1.0
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2.9
1.0
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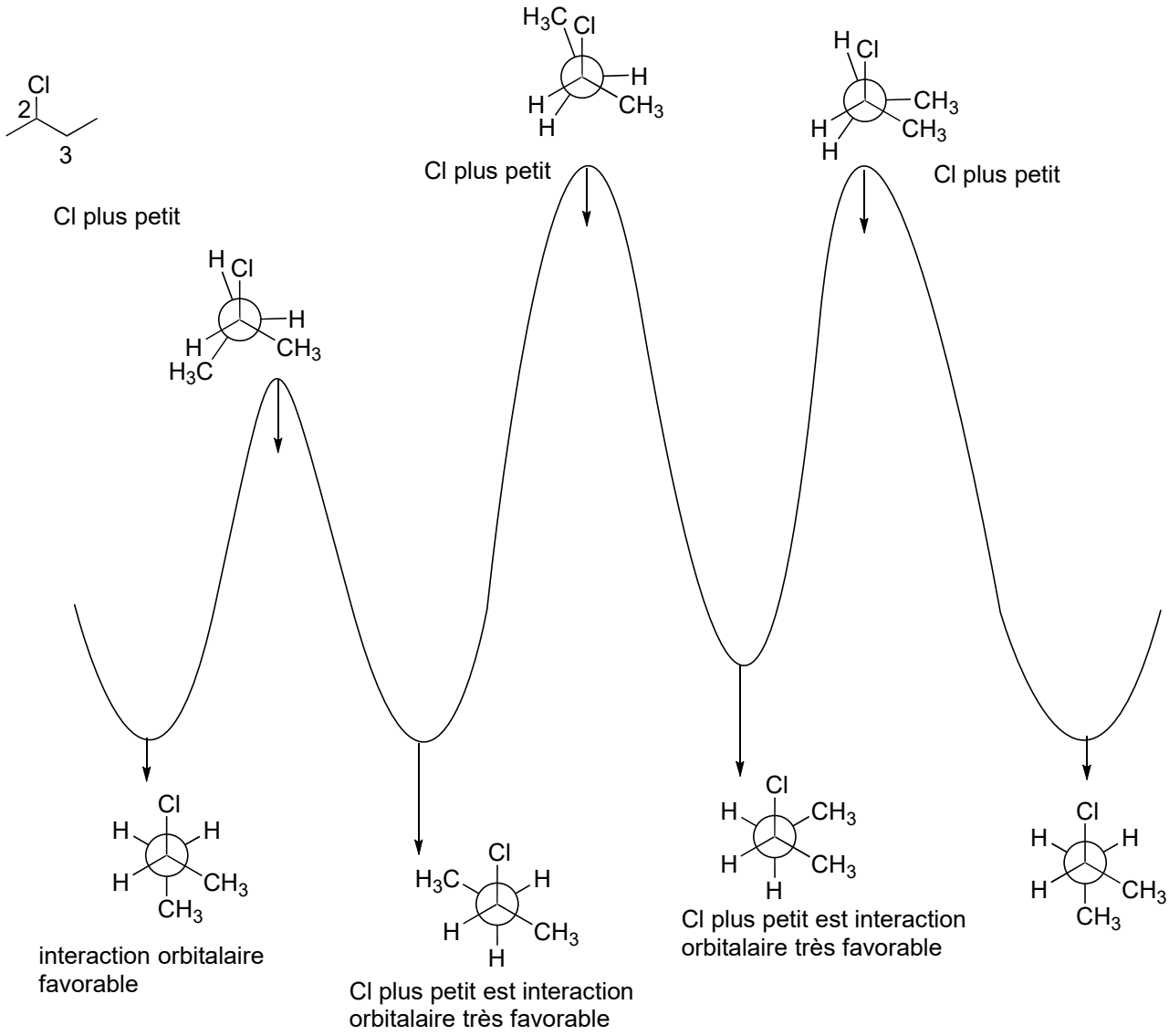
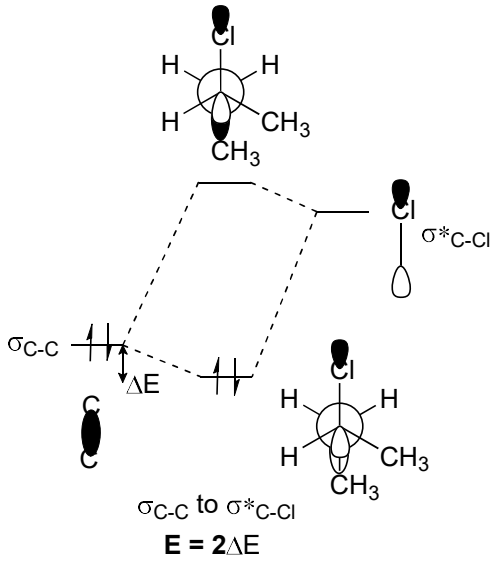
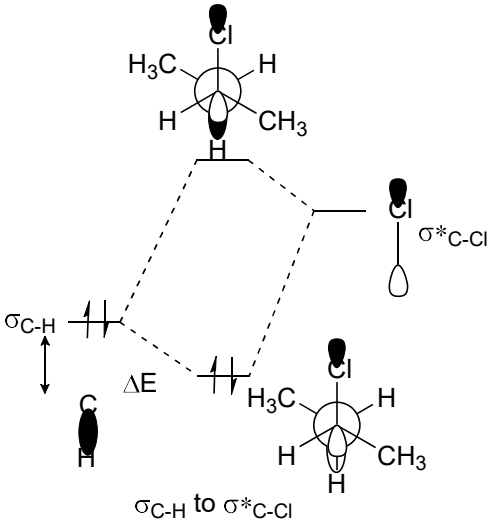


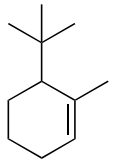
interactions orbitalaires favorables supplémentaires pour Cl:





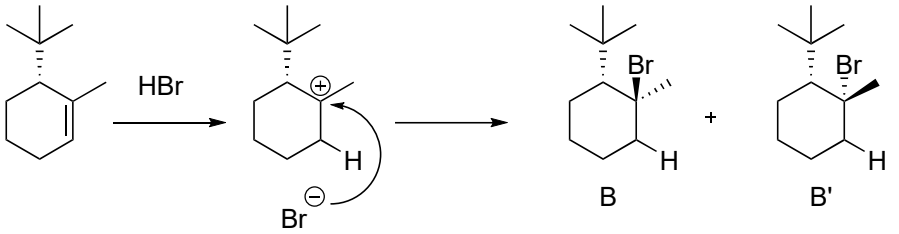
légèrement meilleur (H plus électropositif que C)

11)



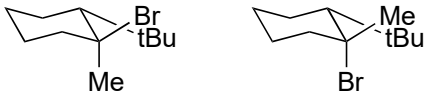
HBr → B + B'

A



Formation du carbocation le plus stable

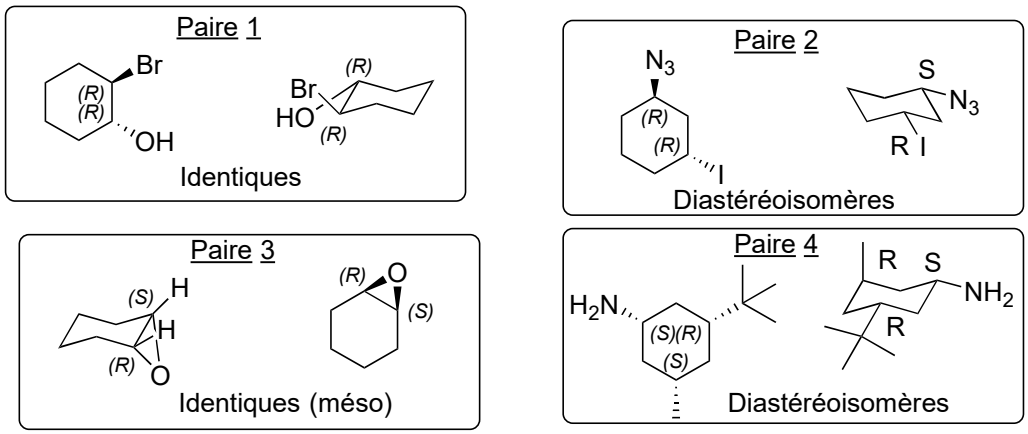
B et B' sont diastéréoisomères

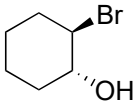


B B'

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

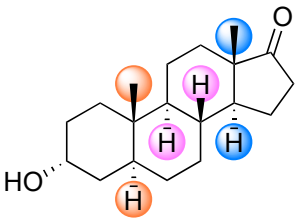
12)

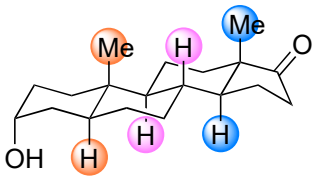




(1*R*,2*R*)-2-bromocyclohexan-1-ol

13)



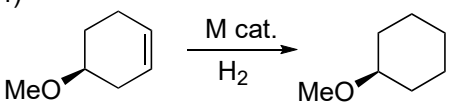


trans

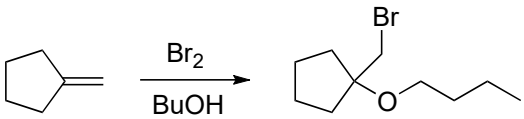
trans

trans

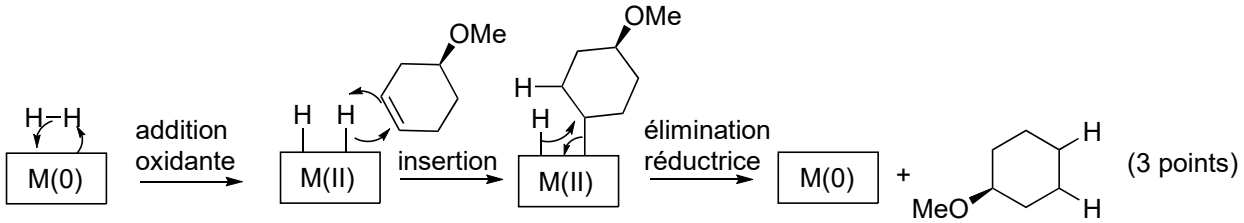
14)



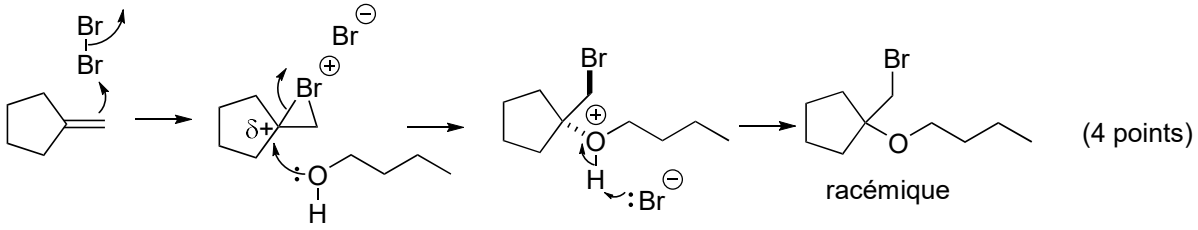
M = Pd, Pt, Ni or Rh



racémique (2 points)



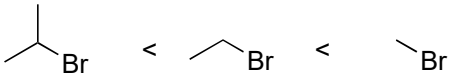
(3 points)



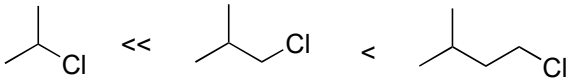
racémique (4 points)

charge partielle en tertiaire
Attaque opposée à Br

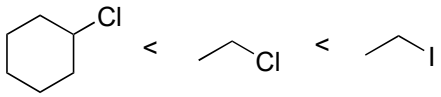
15)

a)  (2 points)

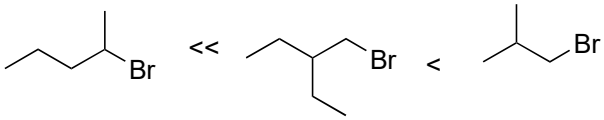
effet stérique sur l'état de transition: les substituants ralentissent la réaction

b)  (2 points)

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

c)  (2 points)

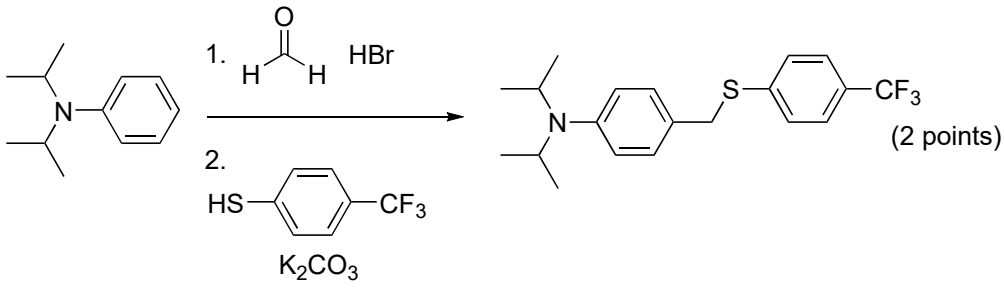
1) effet stérique: secondaire plus lent que primaire
2) L'iode est un meilleur groupe partant (électrons stabilisés sur grand atome)

d)  (2 points)

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

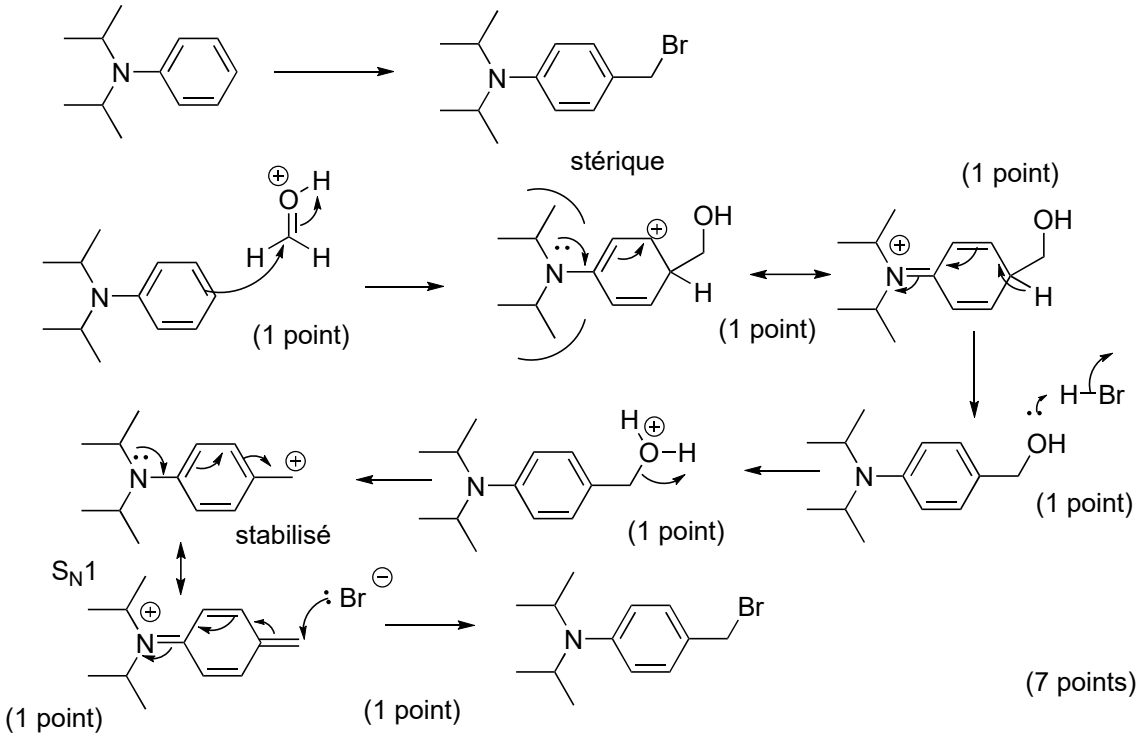
16)

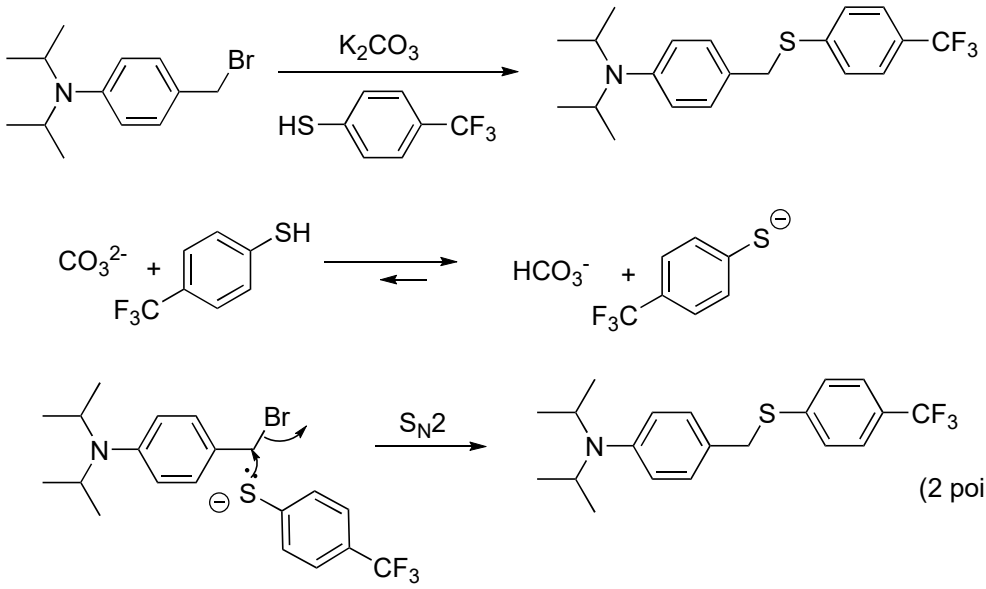
(1)



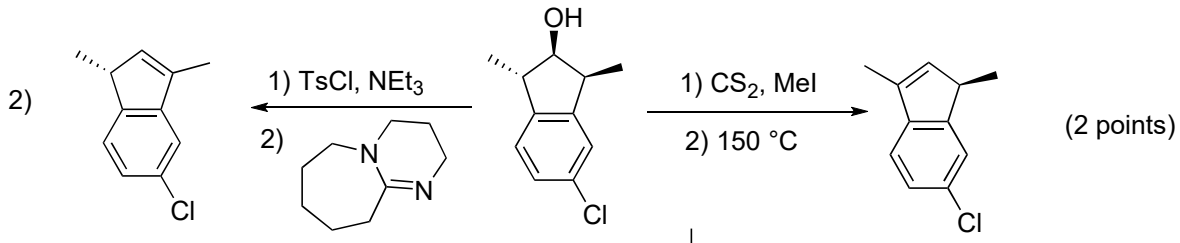
(2 points)

mécanisme



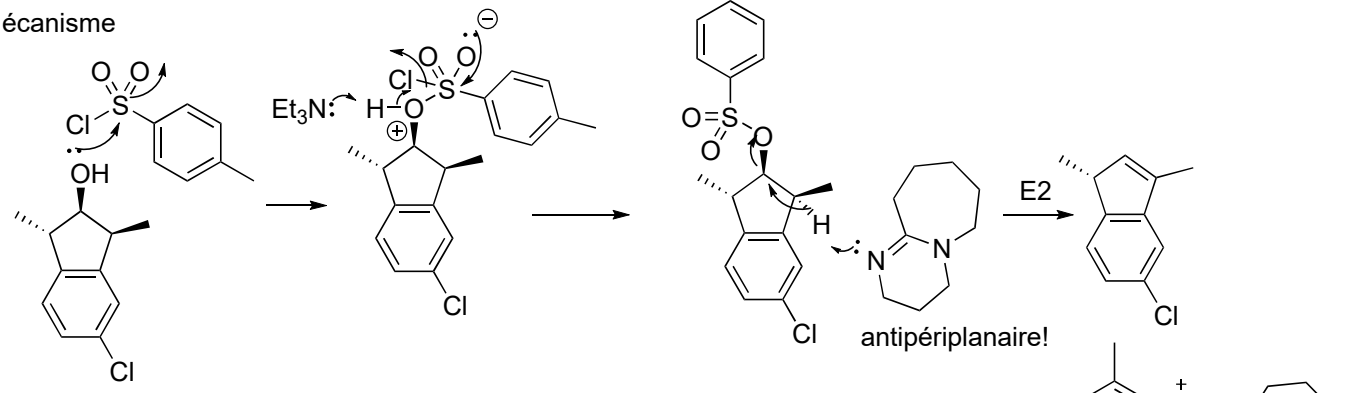


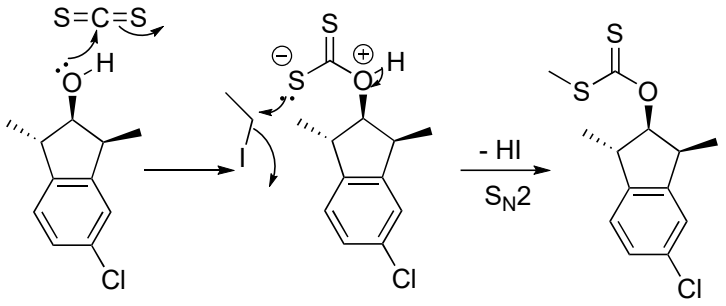
17)



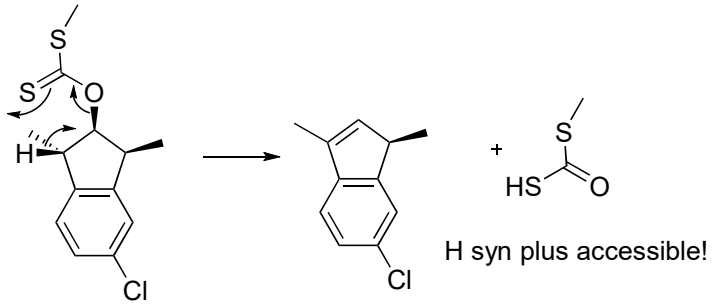
(2 points)

mécanisme

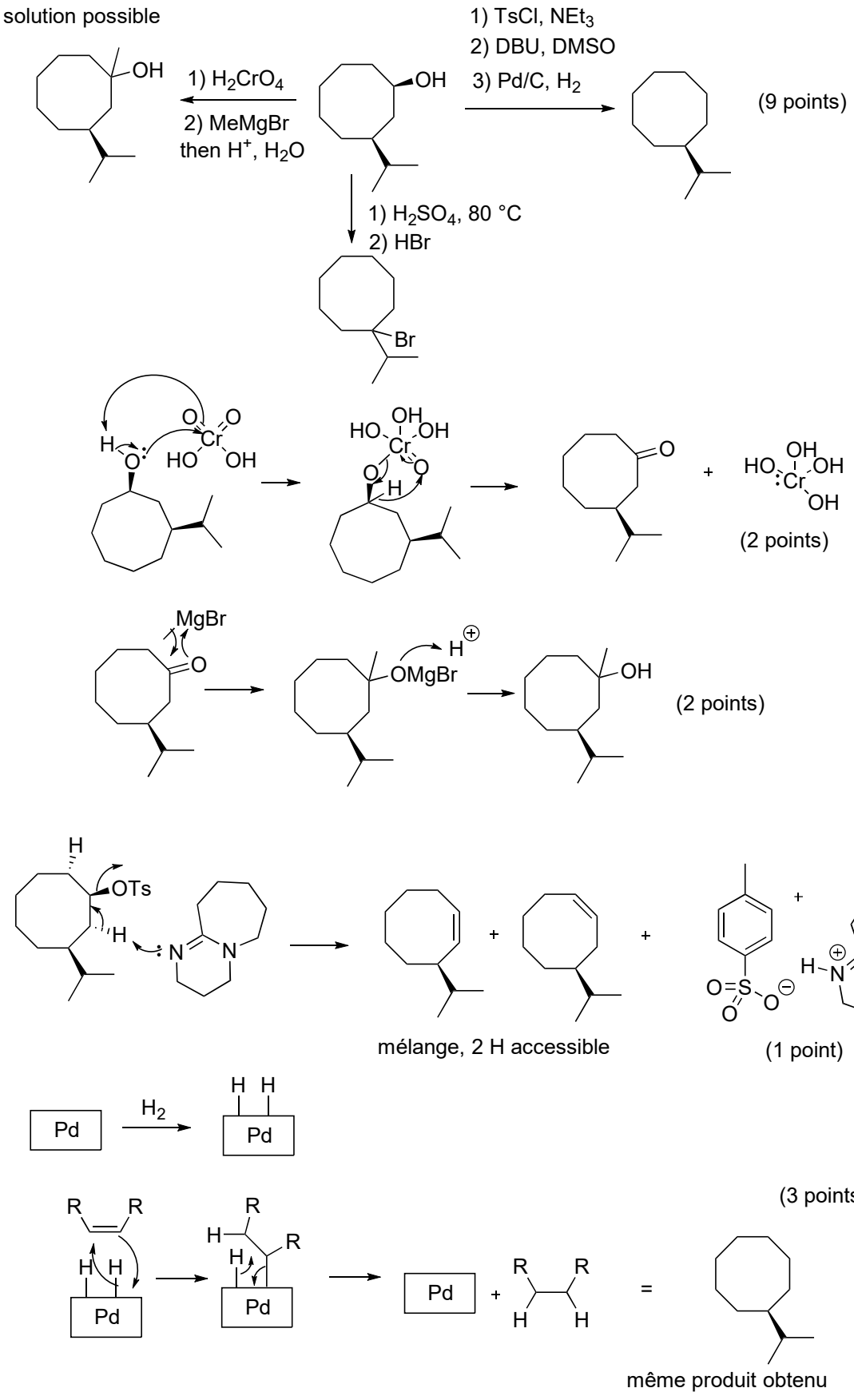


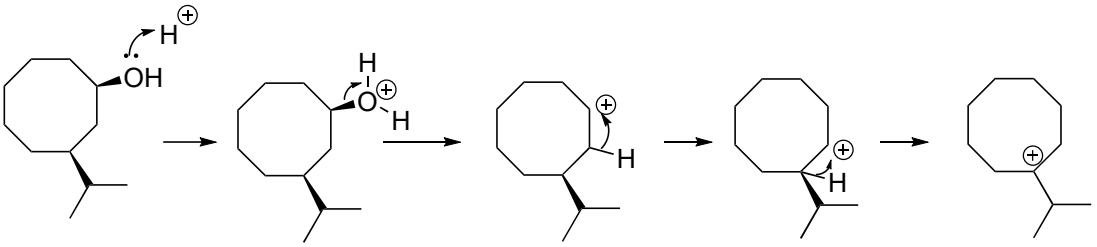


(6 points)

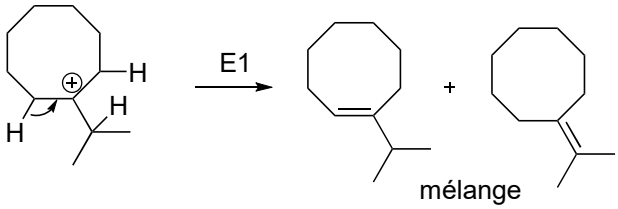


18)


solution possible
1) TsCl, NEt3
2) DBU, DMSO
3) Pd/C, H2
(9 points)
1) H2CrO4
2) MeMgBr
then H+, H2O
1) H2SO4, 80 °C
2) HBr
(2 points)
(2 points)
mélange, 2 H accessible
(1 point)
(3 points)
même produit obtenu

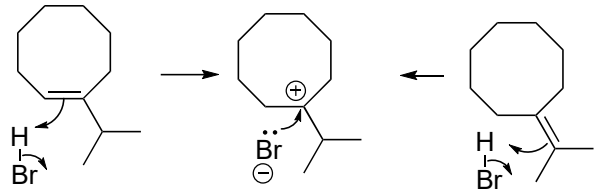


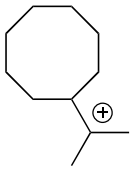
tertiaire: plus stable



(4 points)

mélange



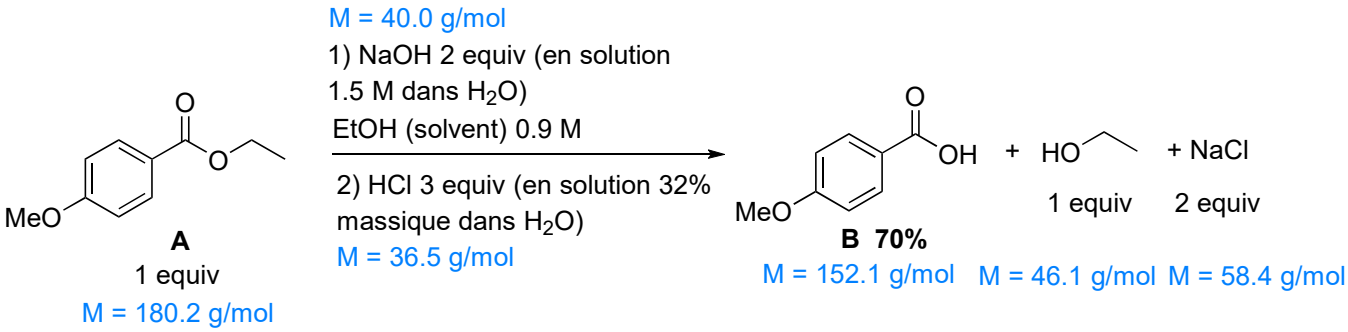


(2 points)

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

19)

La réaction ci-dessous a été faite durant les TP d'automne 2022.
1) Calculer une valeur estimée pour l'économie d'atomes, le facteur E et le PMI (8 points)
2) Evaluer de façon qualitative le procédé par rapport aux 12 principes de la chimie verte (5 points).



Purification:
1) Filtration: H_2O (2.5 x volume du solvent de la reaction)
2) Crystalisation: H_2O (1 x volume du solvent de la reaction) et EtOH (1x volume de la reaction),
3) Filtration: H_2O (2.5 x volume du solvent de la reaction)

EtOH: d = 0.79
H_2O: d = 1.0
HCl 32%massique
1.5 M NaOH: d = 1.2

Solution:
1)
Economie d'atomes : Nombre d'atomes des molécules de départ qui se retrouvent dans le produit final.
Ici 25 atomes dans A (C10H12O3), il faut ajouter les molécules qui vont réagir avec et donner de leurs atomes : 3 atomes dans NaOH et 2 atomes dans HCl.
 Atomes des molécules de départ : 25+2+3=30.
Le produit final est B, il a 19 atomes (C8H8O3).
Donc économie d'atomes = 19 / 30 = 63%.

Bilan de masse :
On raisonne sur 1 kg de produit final B. nB=mB/MB= 1000 / 152.1 = 6.57 mol.
On utilise le rendement pour remonter à nA: nA=nB/rendement= 6.57 / 0.7 = 9.38 mol. On a donc mA=nA*MA= 9.38 * 180.2 = 1690 g = 1.69 kg.
On calcul ensuite les quantités des réactifs:
- NaOH (2 equiv.) : nNAOH=2*nA= 2 * 9.38 = 18.76 mol. C'est une solution de 1.5 mol de NaOH par litre d'eau.

Le volume de solution nécessaire pour la réaction est donc VsolNaOH=nNAOH/Cmolaire= (18.76 * 1) / 1.5 = 12.50 L.
On calcule la masse volumique avec la densité : ρsolNAOH=ρeau*d= 1 * 1.2 = 1.2 kg/L.
On en déduit la masse de la solution msolNaOH=VsolNAOH*ρsolNAOH= 12.50 * 1.2 = 15.00 kg. Dans cette solution, on utilise que le NaOH, toute l'eau sera donc du déchet. mNAOH=nNAOH*MNAOH = 18.76 * 40 = 750 g = 0.75 kg. On en déduit la masse d'eau déchet : meaudechet=msolNAOH-mNAOH = 15.00 - 0.75 = 14.25 kg.
- HCl (3 quiv.) : on fait de même. nHCl=3*nA=3*9.38=28.14 mol. Cette fois ci on a une solution massique (on a 0.32 kg de HCl par kg d'eau) ! Il nous faut donc la masse de HCl. mHCl=nHCl*MHCl= 28.14 * 36.5 = 1027.11 g = 1.03 kg.

On a donc msolHCl =mHCl/Cmassique= 1.03 / 0.32 = 3.22 Kg.
Dans cette solution, on utilise que le HCl, toute l'eau sera donc du déchet.
meaudechet=msolHCl-mHCl = 3.22 – 1.03 = 2.19 kg.
On calcule ensuite la quantité de solvant (ici EtOH).
- On a 0.9 mol de A par litre d'ethanol. VEtOHsolvant=nA/Cmolaire= 9.38 / 0.58 = 10.42 L.

ρEtOH=ρEtOH*d = 1 * 0.79 = 0.79 kg/L.
mEtOHsolvant=VEtOHsolvant*ρEtOH = 10.42 * 0.79 = 8.23 kg.
Puis on calcule les quantités des produits non désirés de la réaction (sous-produits) :
- Ethanol (1 equiv.): on a nEtOH=nA= 9.38 mol. mEtOH=nEtOH*MEtOH= 9.38 * 46.1 = 432 g = 0.43 kg.
- NaCl (2 equiv): de même on a nNaCl=2*nA= 2 * 9.38 = 18.76 mol. mNaCl=nNaCl*MNaCl= 18.76 * 58.4 = 1096

- NaCl (2 équiv): de même on a nNaCl=2 nA= 2 * 9.56 = 19.12 mol. mNaCl=nNaCl MNaCl= 19.12 * 58.4 = 1090 g = 1.10 kg.

Enfin on calcule ensuite la quantité de solvants utilisé durant la phase de purification :

- H2O : VH2O=(2.5+1+2.5)*VEtOHsolvant= 6 * 10.42 = 62.52 L. mH2O= 1 * 62.52 = 62.52 kg.
- EtOH : VEtOH=1*VEtOHsolvant= 1 * 10.42 = 10.42 L. ρEtOH=ρEtOH*d = 1 * 0.79 = 0.79 kg/L.

mEtOH=VEtOH*ρEtOH = 10.42 * 0.79 = 8.23 kg.

- On peut faire la somme mpurif= 62.52 + 8.23 = 70.75 kg.

PMI : masse totale de matériel nécessaire (molecule de depart, reactifs, solvant de la reaction, solvant et matériel de purification) pour produire une unité de produit (ici 1 kg).

PMI = (mA + msolNaOH + msolHCl + mEtOHsolvant + mpurif)/1 = 1.69 + 15.00 + 3.22 + 8.23 + 70.75 = 98.89.

Facteur E : Ratio de la masse de déchets produite par rapport à la masse du produit final désiré.

E = (meaudechet + msolvant + msousproduits + mpurif) / 1 = 14.25 + 2.19 + 8.23 + 0.43 + 1.10 + 70.75 = 96.95.

Remarques : valeurs approximatives, des chiffres légèrement différents peuvent être obtenus selon la précision utilisée. Pour le facteur E, les produits de départs convertis ne doivent pas être considérés, sauf si un excès est utilisé.

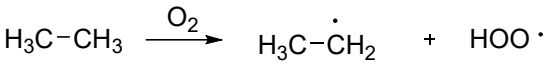
2)

1. Prévention: Déchets pas dangereux, réaction propre, OK.
2. Economie d'atomes: 63%, procédé moyen.
3. Synthèse sans produits toxiques: Attention aux bases et acides forts lors des manipulations! Danger modéré.
4. Produits non toxiques: Bon. Seulement le produit désiré, de l'éthanol et du NaCl après neutralisation.
5. Substances auxiliaires: OK: pas de substances auxiliaires pour la réaction, de grande quantités de solvants utilis és pour la purification, mais l'eau et l'éthanol sont des solvants verts.
6. Energie minimale: OK, réaction à température ambiante.
7. Matière première renouvelable: Difficile à juger sans connaitre l'origine du produit de départ, mais probablement dérivé du pétrole... Réactifs OK (NaOH, HCl abondants).
8. Synthèse directe: OK pas de manipulations supplémentaires.
9. Catalyseurs: pas nécessaire ici, réaction rapide.
10. Produits dégradable: difficile sans informations, mais probablement limité ici.
11. Contrôle des réactions: Attention, certaines étapes sont exothermiques (acides forts, bases, neutralisation), né cessitant un contrôle de la température.
12. Sécurité: Protection contre les projections corrosives (acides-bases), lunettes de protections, blouses, et gants!

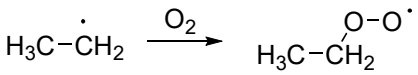
[barème: 2 points pour l'économie d'atome, 3 points pour le facteur E, 3 points pour le PMI, 5 points pour l'é valuation qualitative]

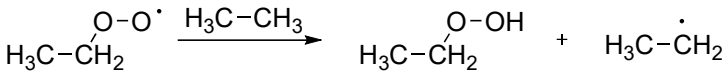
20) Proposez un mécanisme plausible et détaillé pour la combustion de l'éthane

initiation 1

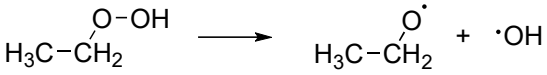


propagation 1

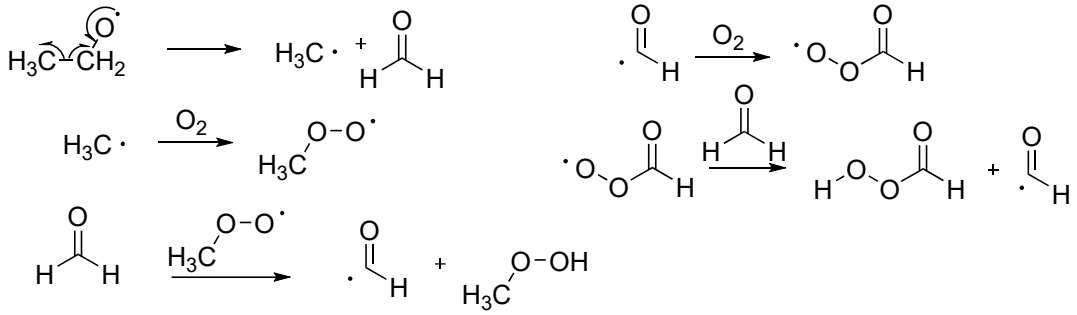




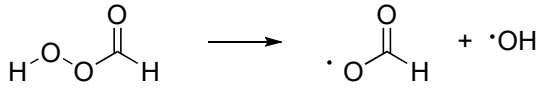
initiation 2



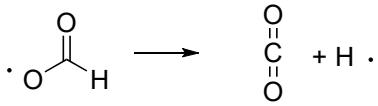
propagation 2



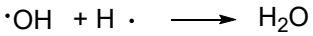
initiation 3

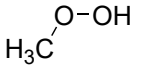


propagation 3



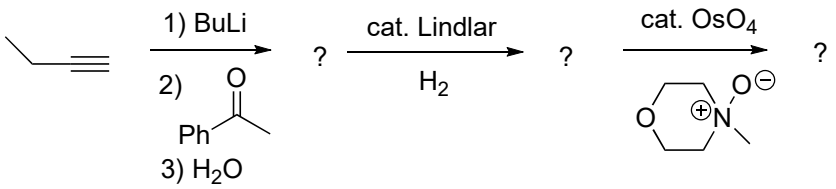
terminaison (exemples, beaucoup de possibilités!)

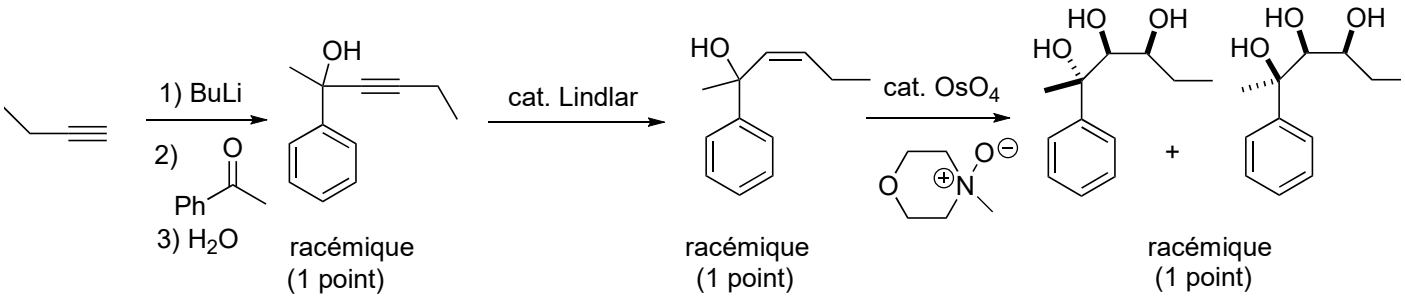


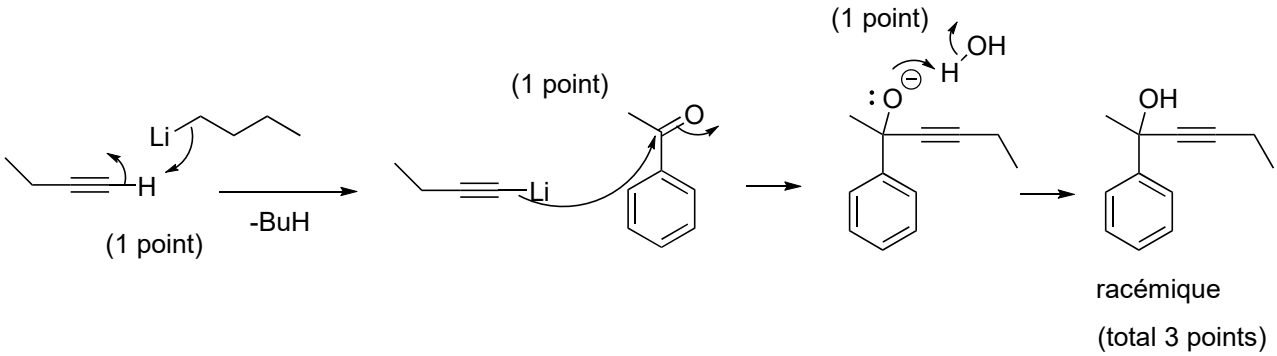
La réaction de  continue de façon similarie jusqu'au CO_2. Bien sûr, il y a beaucoup d'alternatives légèrement différentes.

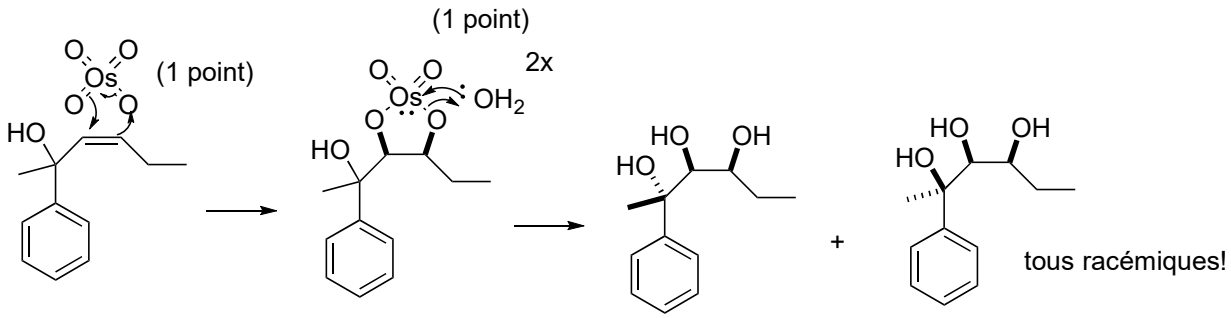
[barème: 15 points pour un mécanisme complet sans erreur conduisant au CO2 et à l'eau (correction en mode négatif, -1 point par erreur). Il y a beaucoup de possibilités légèrement différentes de celles données dans cette solution. Merci de contacter un assistant si vous avez un doute sur votre solution.]

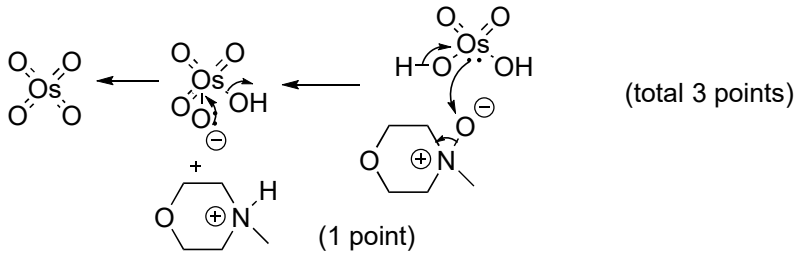
21) Compléter les réactions suivantes et donner les mécanismes. Préciser si le produit est obtenu pur ou comme un mélange d'isomères.





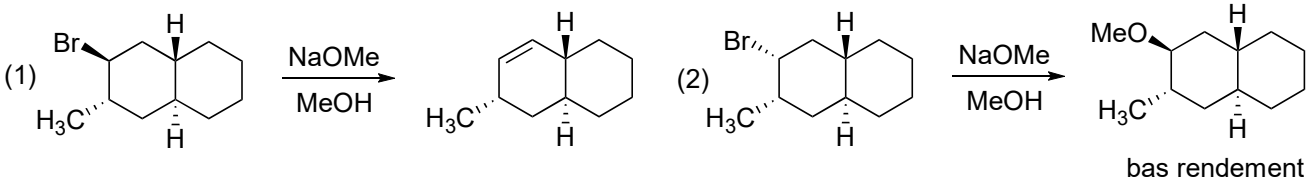


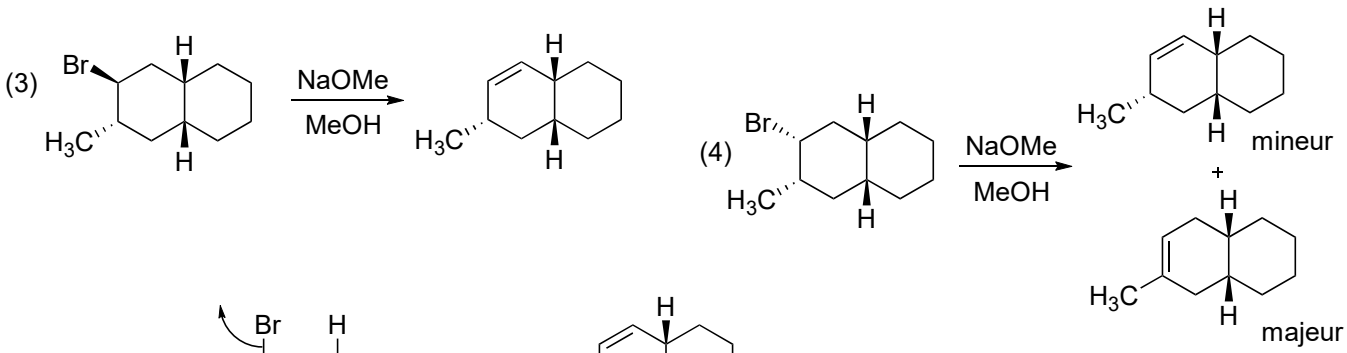


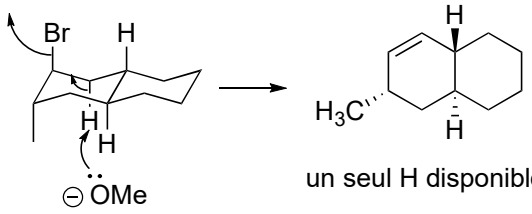


[barème: 3 points pour les réponses (0.5 point pour la réponse si le mélange n'est pas précisé), 9 points pour le mécanisme]

22) Rationaliser la formation des produits observés en vous basant sur le mécanisme des réactions. Comment pourriez-vous inverser la régiosélectivité dans la réaction (4)?

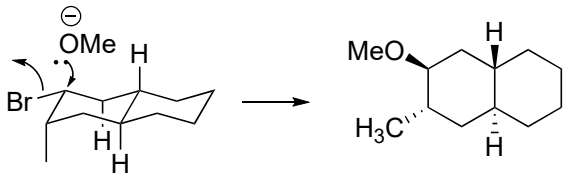






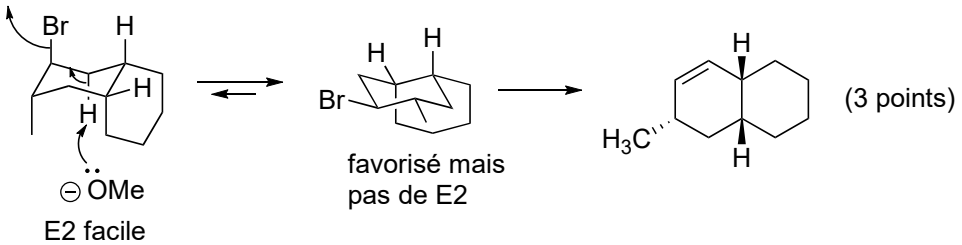
(3 points)

un seul H disponible pour E2



E2 pas possible, S_N2 lente

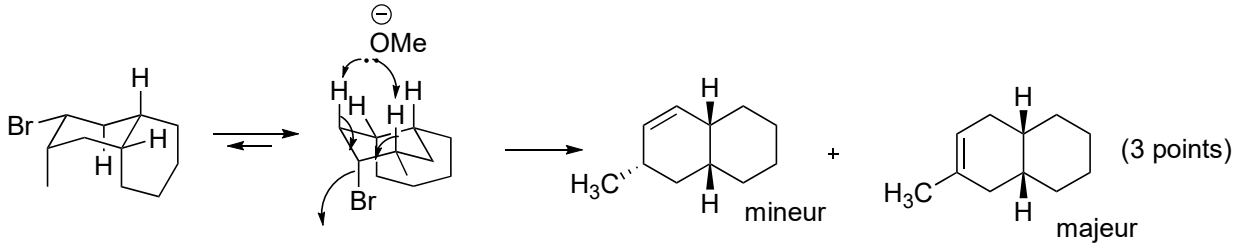
(3 points)



favorisé mais pas de E2

E2 facile

(3 points)



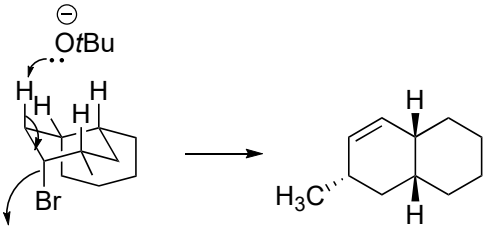
E2 facile

mineur

plus stable (trisubstitué)

(3 points)

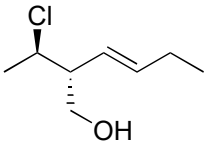
avec KO*t*Bu

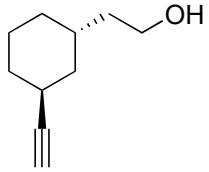


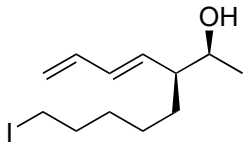
H secondaire stériquement favorisé

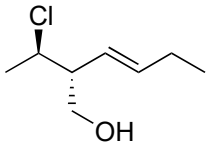
(2 points)

23) Donner la nomenclature systématique des composés suivants.

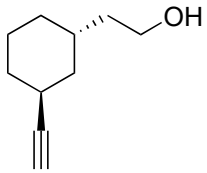




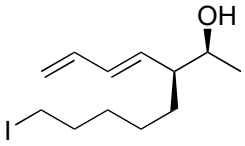




(*R*,*E*)-2-((*R*)-1-chloroethyl)hex-3-en-1-ol (6 points)



2-((1*S*,3*S*)-3-ethynylcyclohexyl)ethan-1-ol (5 points)



(2*S*,3*S*)-3-((*E*)-buta-1,3-dien-1-yl)-8-iodooctan-2-ol (6 points)

(old : (2*S*,3*S*,*E*)-3-(5-iodopentyl)-hepta-4,6-dien-2-ol)

[barème: 1 point pour la chaine principale, 1 point pour la numérotation, 1 point par substituant, 1 point par stéré ocentre/géométrie d'oléfines]