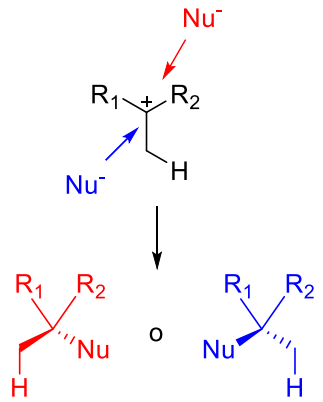
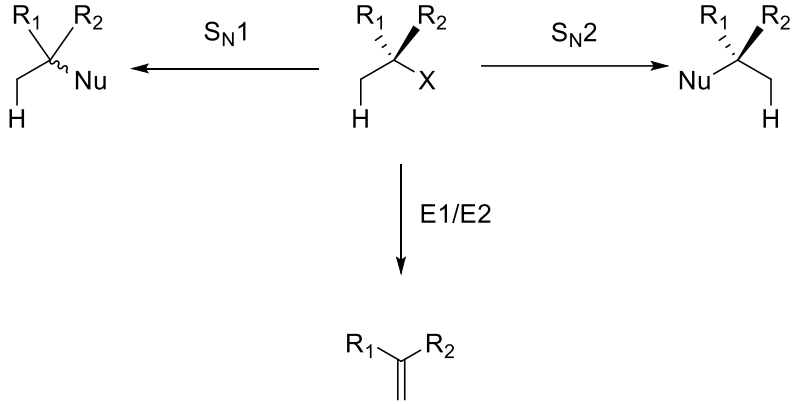
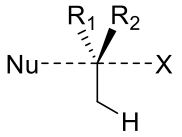
Sostituzioni Nucleofile Alifatiche

Meccanismo S_N1:
formazione del C^+



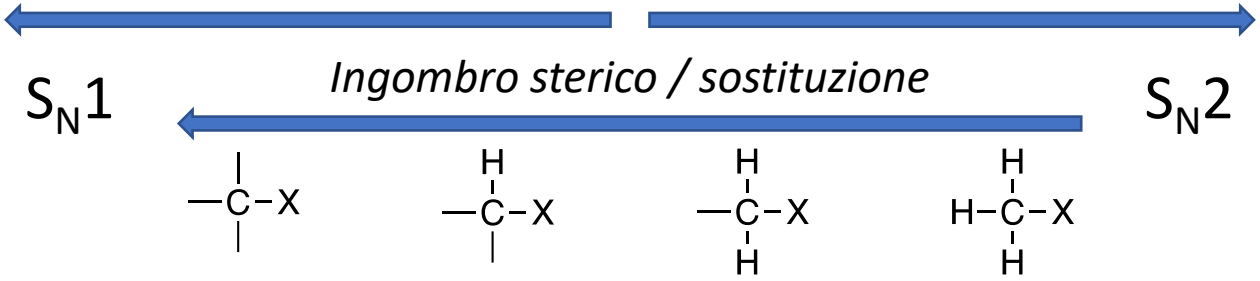


Meccanismo S_N2:
senza intermedio

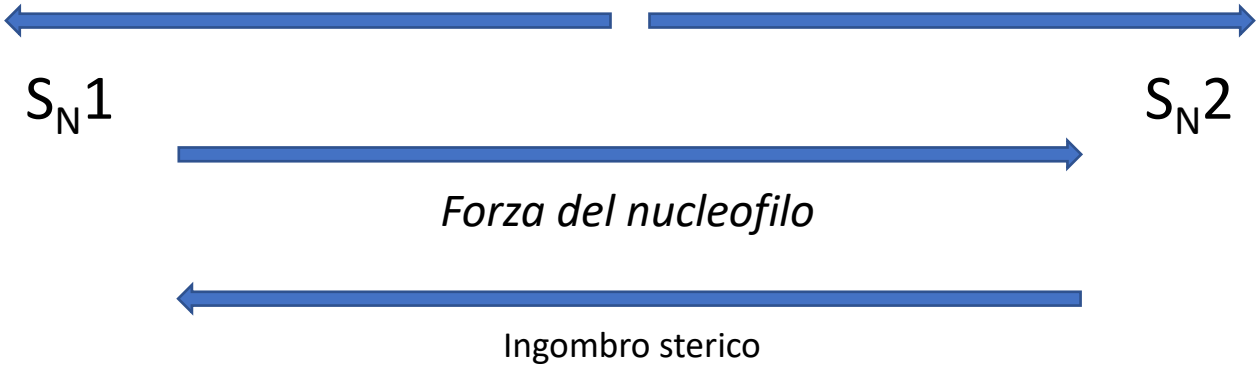


S_N1: favorita quando	S_N2: favorita quando
Carbocatione stabile	Minor ingombro sterico
Nucleofilo debole	Nucleofilo forte
Solvente polare e protico	Solvente polare aprotico

Effetto dell'alogenuro alchilico



Effetto del nucleofilo



Densità di carica positiva H_3O^+ neutro H_2O negativa OH^-

Basicità F^- OH^- NH_2^- CH_3^-

Fattore preponderante in solventi polari aprotici

Elettronegatività F^- Cl^- Br^- I^-

In solventi polari protici

In solventi polari aprotici

Effetto del gruppo uscente

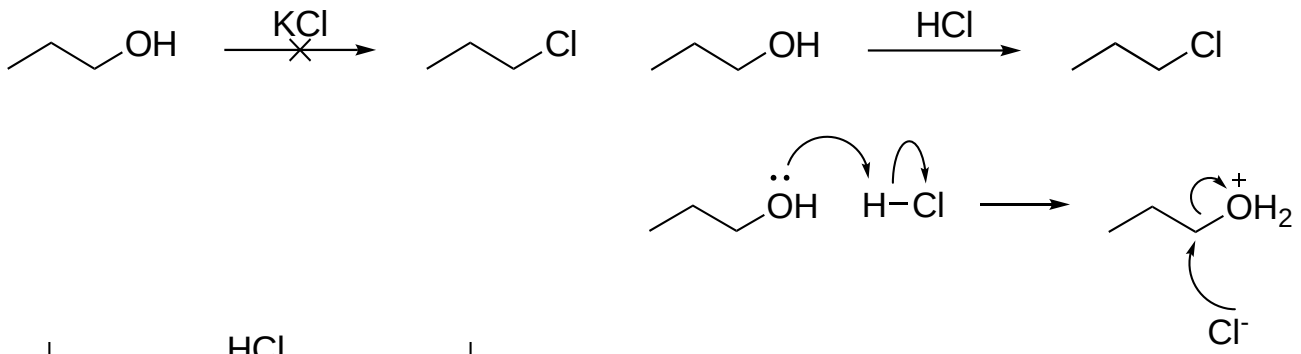
S_N1 S_N2

Forza del gruppo uscente

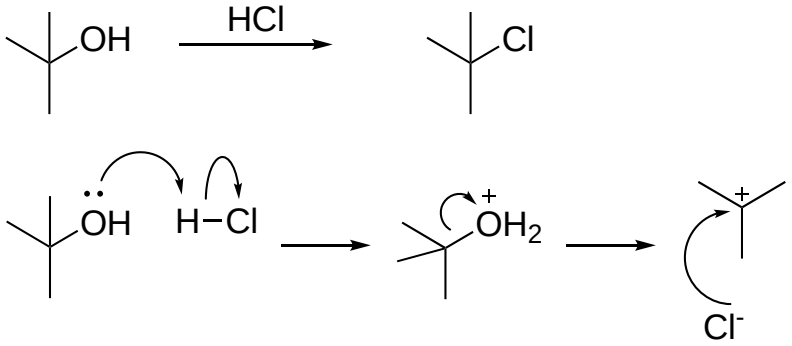
Basicità

La forza di un gruppo uscente può essere aumentata aggiungendo un acido

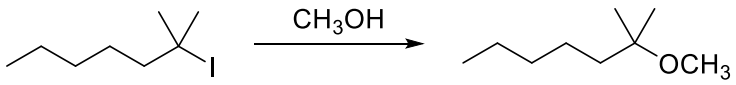
S_N2

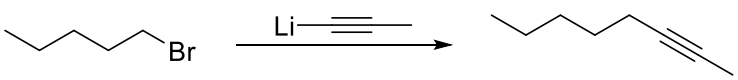


S_N1

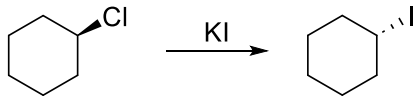


SN_1 o SN_2?

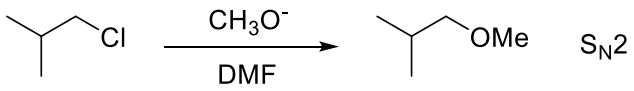




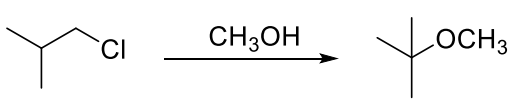
S_N2



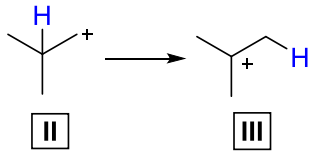
S_N2

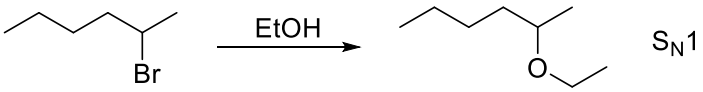


S_N2

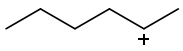


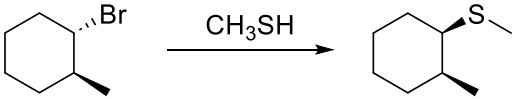
S_N1



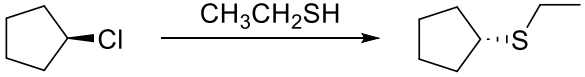


S_N1



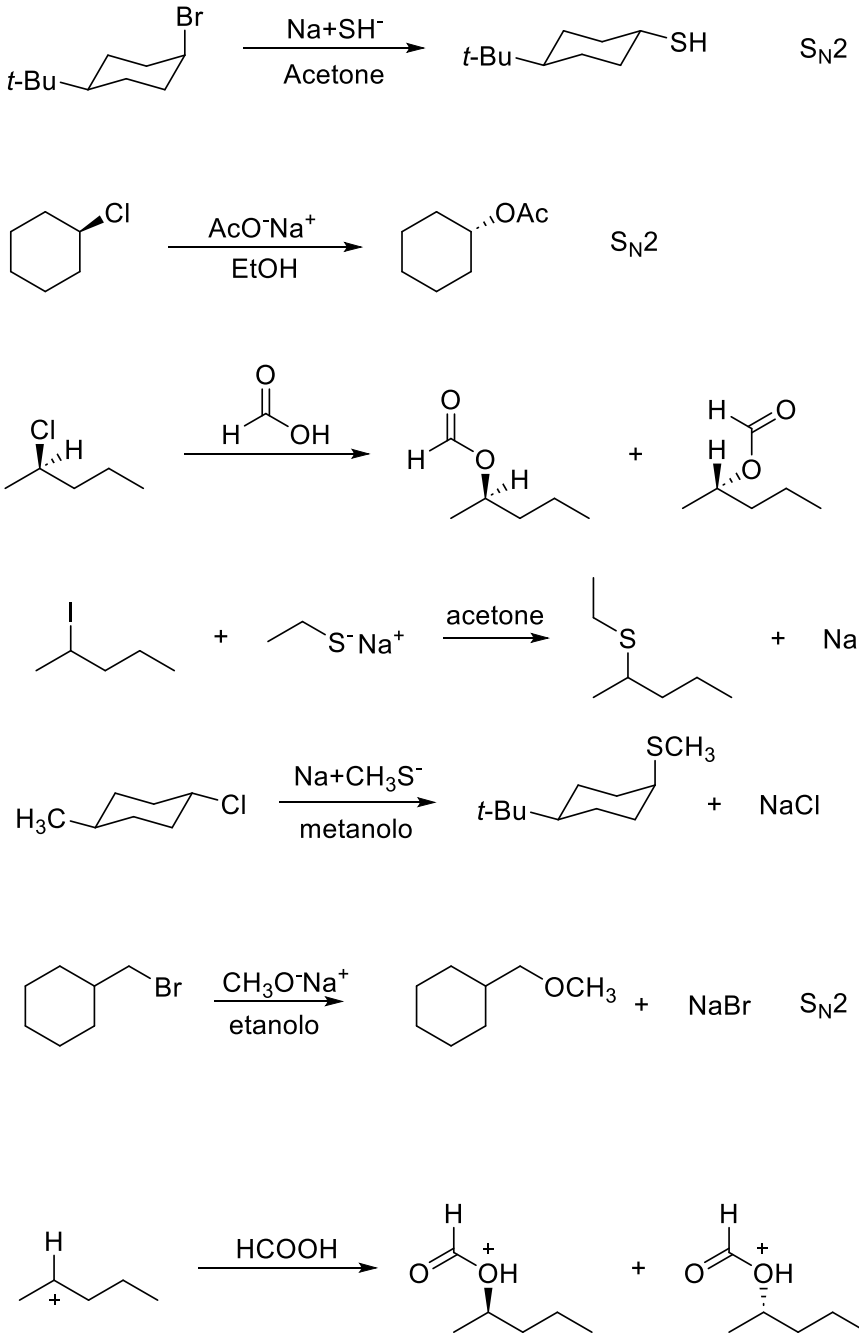


S_N2



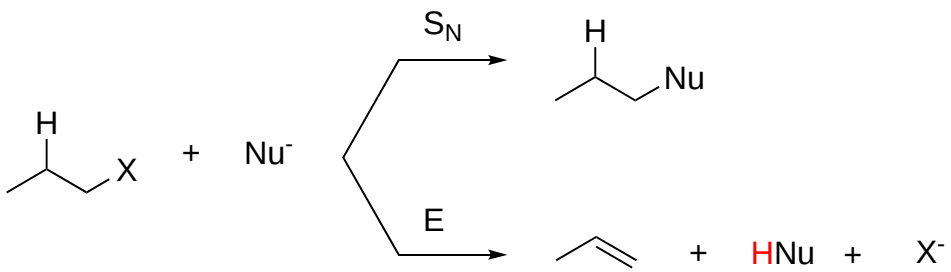
S_N2

SN_1 o SN_2?


Br
t-Bu
Na+SH-
Acetone
t-Bu
SH
SN2
Cl
AcO-Na+
EtOH
OAc
SN2
Cl
H
O
H
OH
H
O
O
H
+
H
O
H
O
SN1
I
+
S-Na+
acetone
S
+
NaI
SN2
H3C
Cl
Na+CH3S-
metanolo
SCH3
t-Bu
+
NaCl
SN2
Br
CH3O-Na+
etanolo
OCH3
+
NaBr
SN2
H
+
HCOOH
H
O
+
OH
+
H
O
+
OH

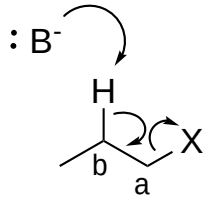
Eliminazioni

Nu^- è anche una base



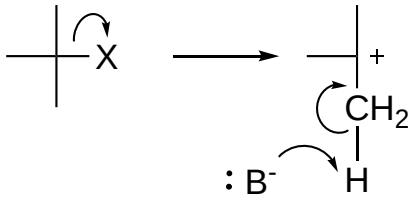
E1: favorita quando	E2: favorita quando
Carbocatione stabile	Base forte
Solvente polare e protico	Solvente polare aprotico
	Angolo 180° tra H e X

E2 concertata



Alogenuro alchilico primario

E1 a stadi

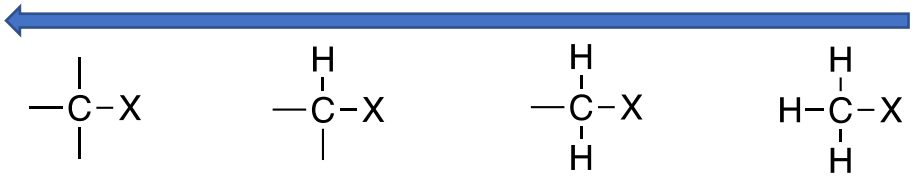


Alogenuro alchilico terziario

E1 E2

Effetto dell'alogenuro alchilico

Ingombro sterico / sostituzione



Effetto della base

Forza della base

(specialmente in solventi non ionizzanti)

Effetto del solvente

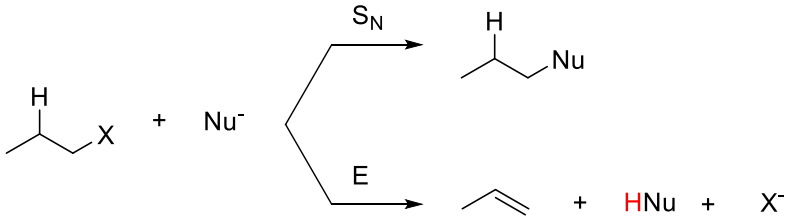
Solventi polari protici Solventi apolari

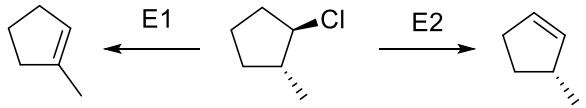
Effetto del gruppo uscente

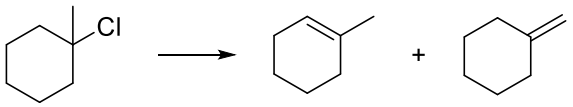
Gruppi uscenti carichi negativamente → **Regola di Zaitsev:** alchene più sostituito

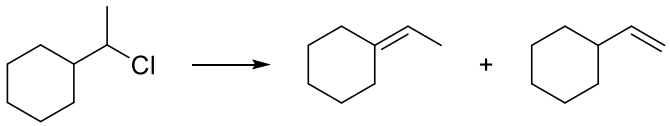
Gruppi uscenti carichi positivamente→ **Regola di Hofmann:** alchene meno sostituito

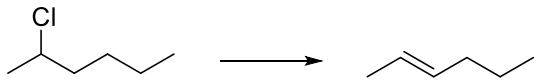
Scrivere i prodotti di eliminazione

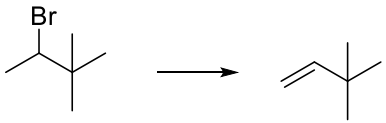


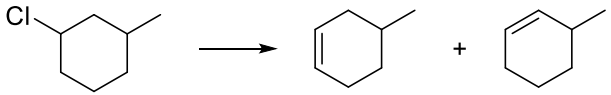


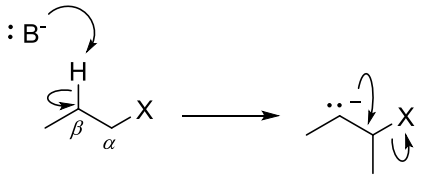


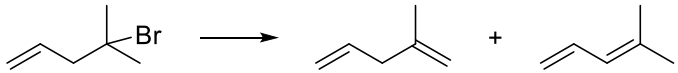






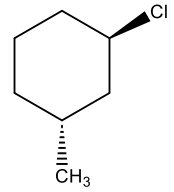




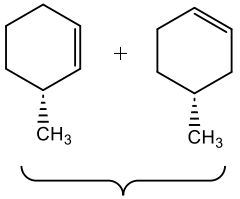


Nucleofilo/Base	Alogenuro 1°	Alogenuro 2°	Alogenuro 3°
R^-	S_N2	S_N2+ E2	E2
	S_N2	S_N2+ E2	E2
$R\text{-}CH_2O^-$ OH^-	S_N2	S_N2+ E2	E2
R_3CO^-	E2	E2	E2
NH_3 RNH_2	S_N2	S_N2+ E2	E2
CN^- $RCOO^-$ N_3^-	S_N2	S_N2	E2
RSH	S_N2	S_N2	S_N1
Cl^- Br^- I^-	S_N2	S_N2	S_N1
ROH H_2O	Non reagisce	S_N1	S_N1

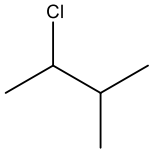
Per ciascuno dei seguenti alogenuri alchilici scrivere tutti i possibili prodotto di eliminazione ed indicare quello predominante



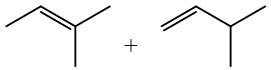
(a)



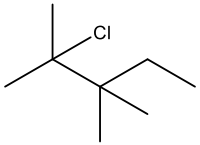
paragonabile



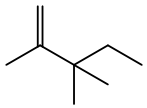
(b)

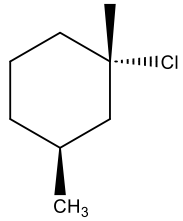


principale

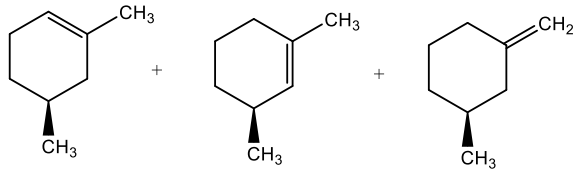


(c)

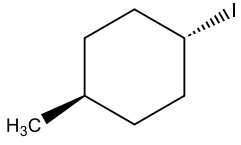




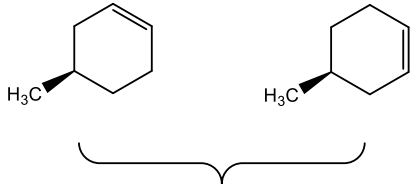
(d)



principale-paragonabile

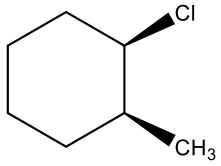


(e)

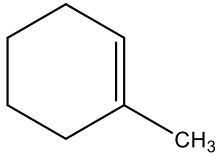


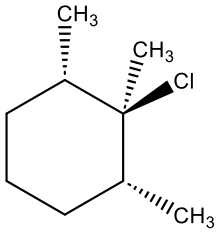
paragonabile

Per ciascuno dei seguenti alogenuri alchilici ciclici scrivere il principale prodotto di eliminazione E2.

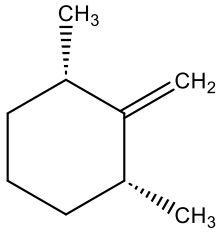


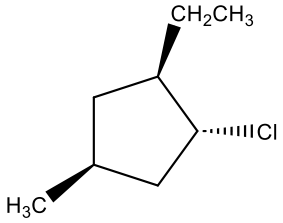
(a)



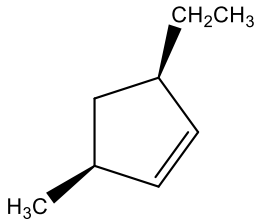


(b)

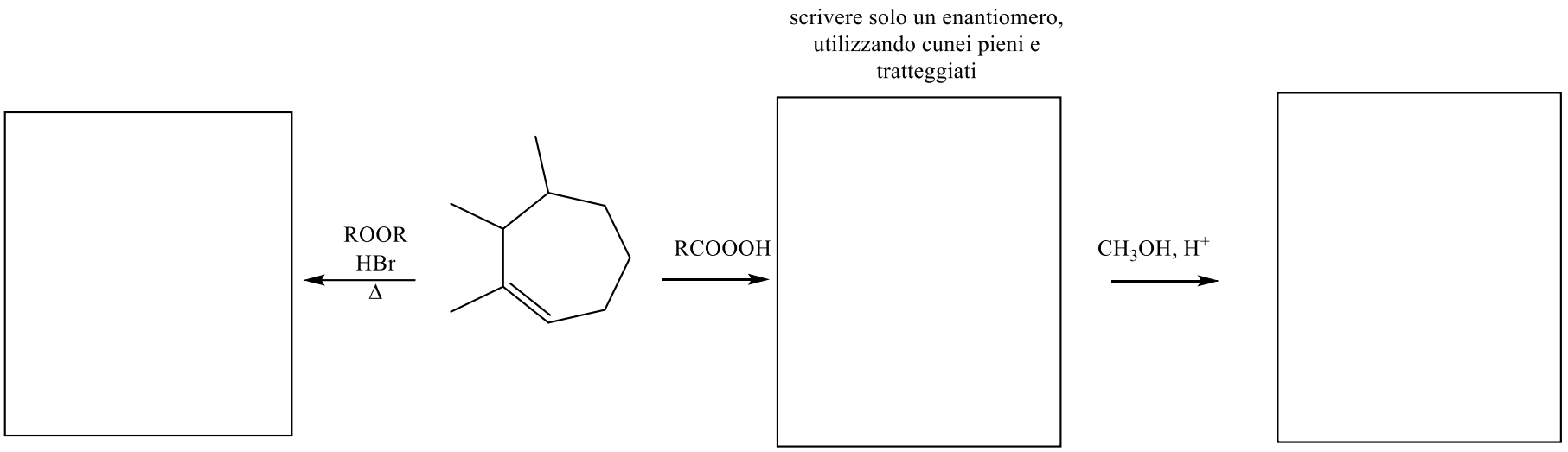




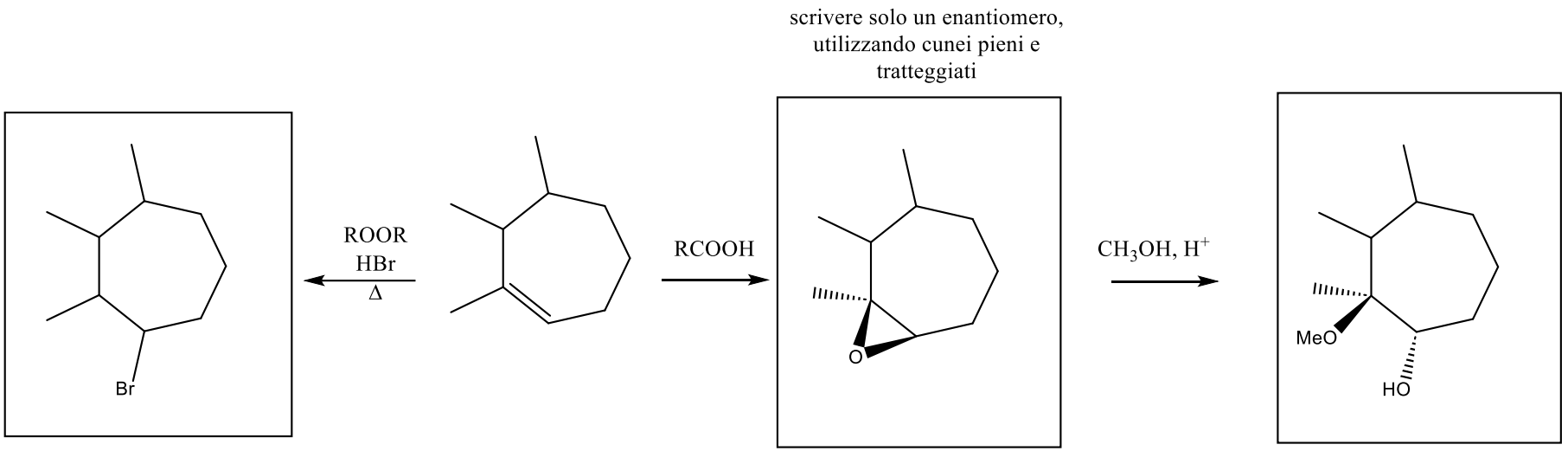
(c)



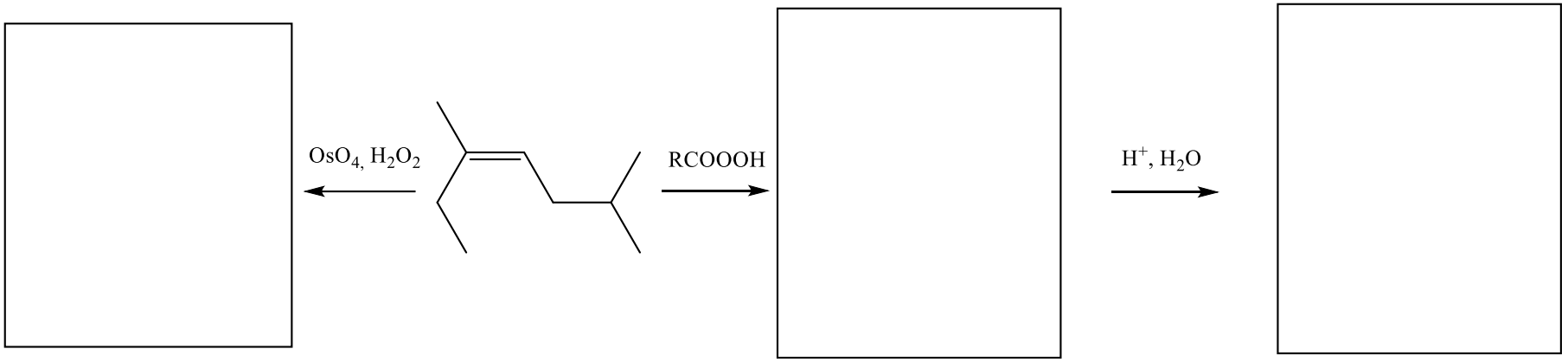
Esercizio d'esame: completare gli schemi di reazione inserendo negli appositi riquadri i prodotti formati



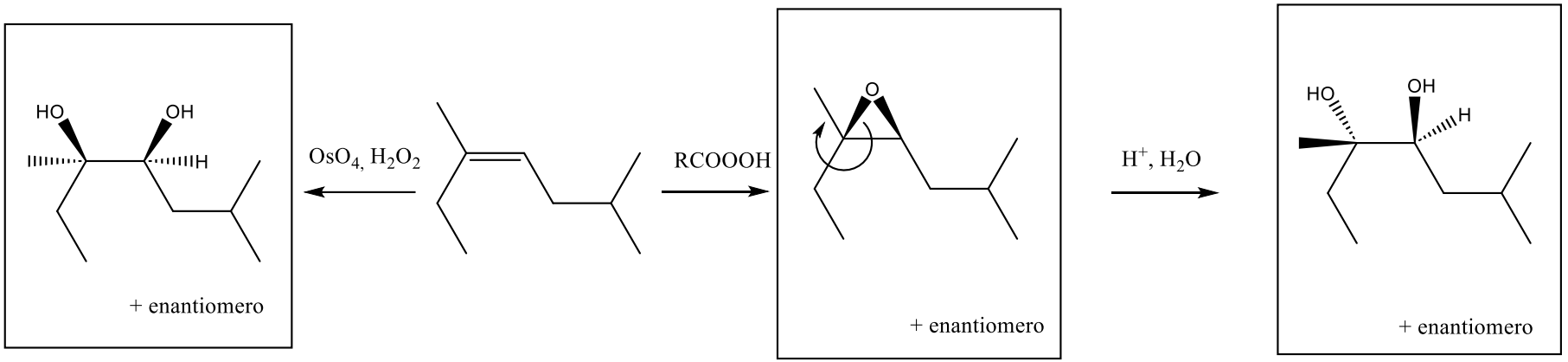
Esercizio d'esame: completare gli schemi di reazione inserendo negli appositi riquadri i prodotti formati



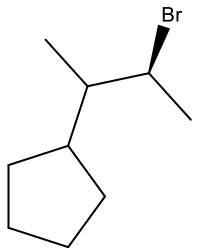
Esercizio d'esame: inserire i prodotti mancanti negli appositi riquadri, avendo cura di rappresentare nelle strutture la corretta stereochimica con l'uso di cunei pieni e tratteggiati.



Esercizio d'esame: inserire i prodotti mancanti negli appositi riquadri, avendo cura di rappresentare nelle strutture la corretta stereochimica con l'uso di cunei pieni e tratteggiati.



Esercizio d'esame: completare gli schemi di reazione con i prodotti formati in prevalenza nelle rispettive trasformazioni, riportando nelle strutture le corrette informazioni stereochimiche e eventualmente implicate.



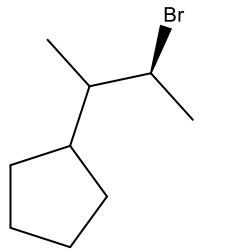
EtOK

KCN
DMSO

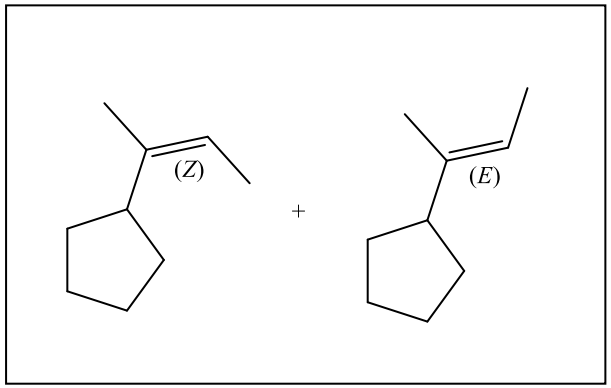
(trascurare i prodotti di sostituzione)

1) O_3
2) H_2O_2

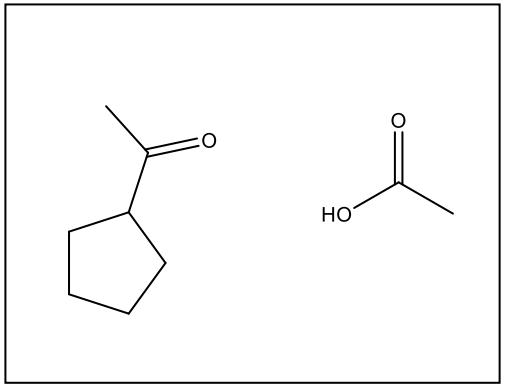
Esercizio d'esame: completare gli schemi di reazione con i prodotti formati in prevalenza nelle rispettive trasformazioni, riportando nelle strutture le corrette informazioni stereochimiche e eventualmente implicate.



EtOK



1) O_3
2) H_2O_2



KCN
DMSO

(trascurare i prodotti di sostituzione)