

CARBENI ED ESERCIZI RIPASSO

LEZIONE 8

CARBENI :CR₂

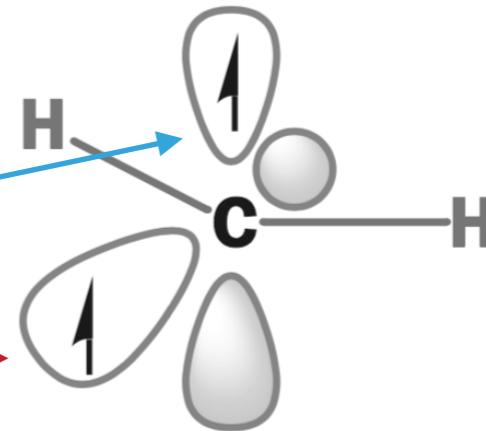
- ▶ specie neutre
- ▶ C sp² con solo 6 elettroni di valenza

Due tipi di carbeni:

- ▶ tripletto: angolo di legame 130-150°

1 e⁻ nell'orbitale p

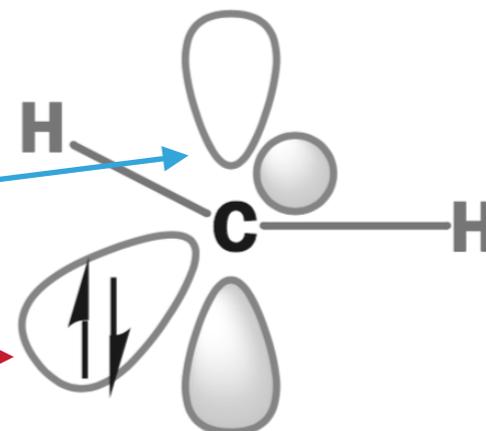
1 e⁻ nell'orbitale sp²



- ▶ singoletto: angolo di legame 100-110°

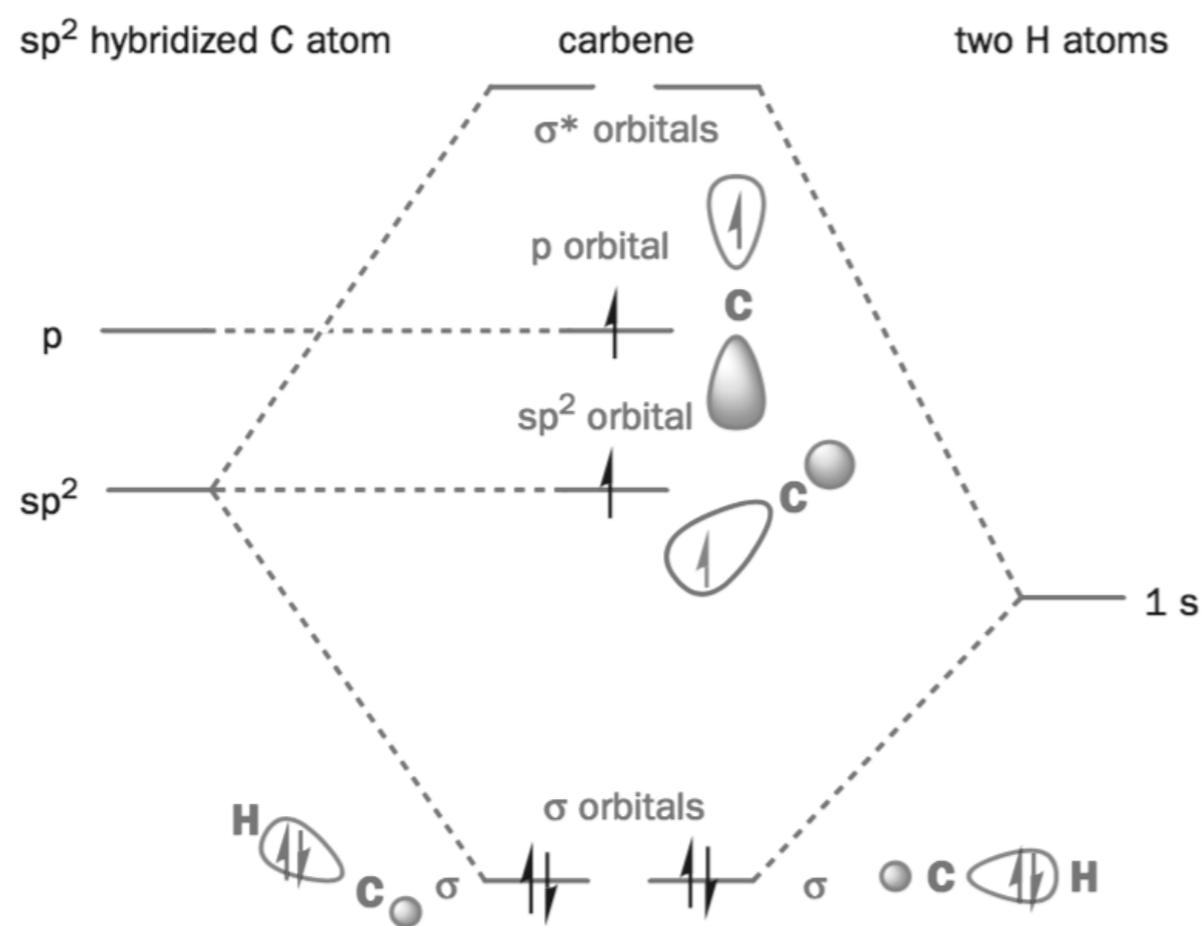
orbitale p vuoto

orbitale di non legame sp² pieno

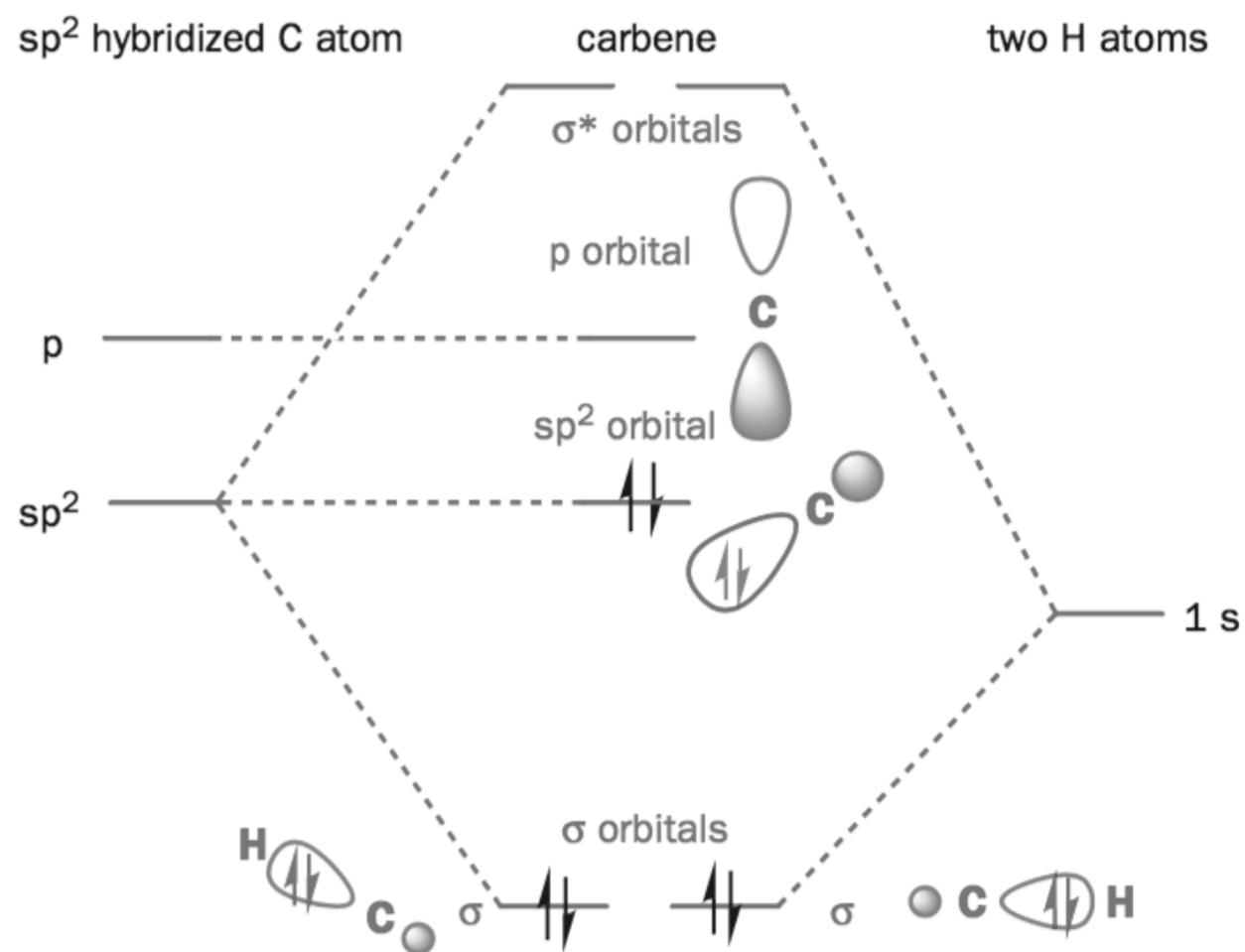


CARBENI :CR₂

carbene tripletto

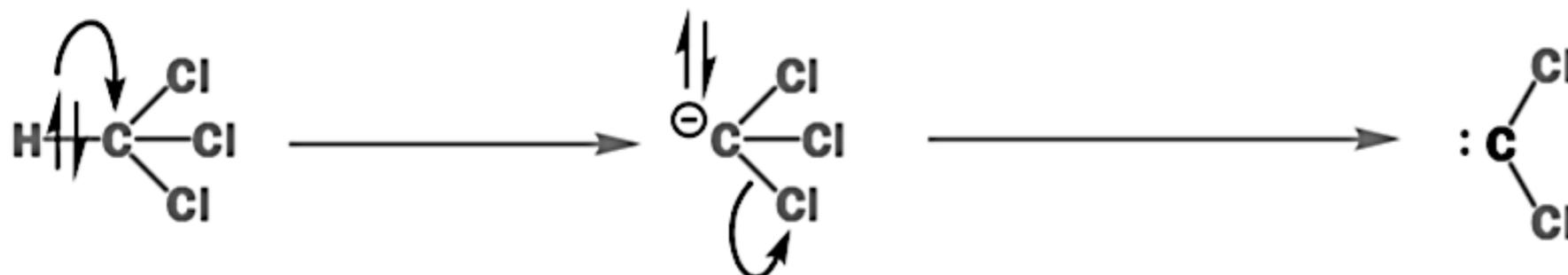


carbene singoletto

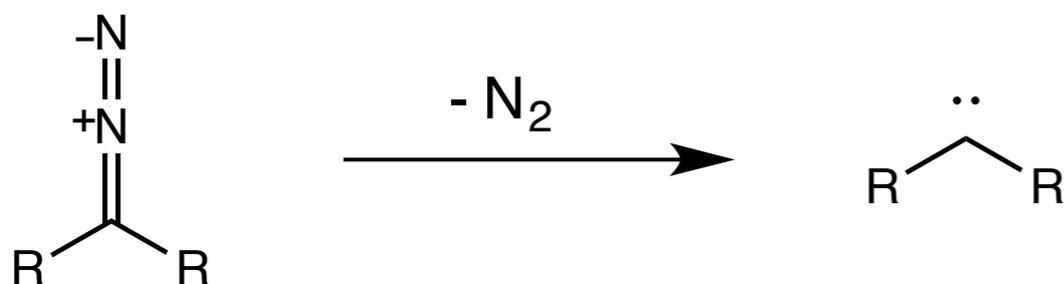


SINTESI DEI CARBENI

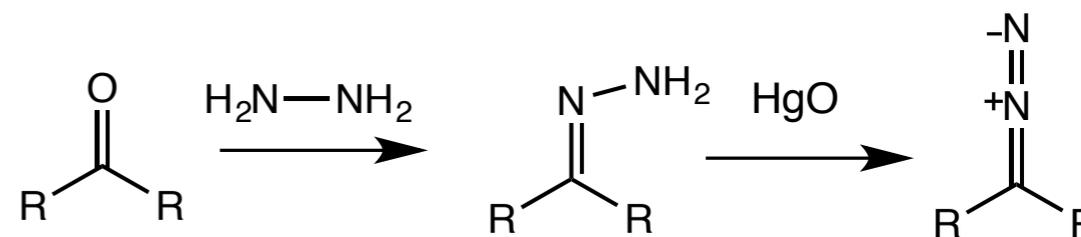
- ▶ Dealogenazione di dialogenoalcano geminale:



- ▶ Sintesi da diazocomposti

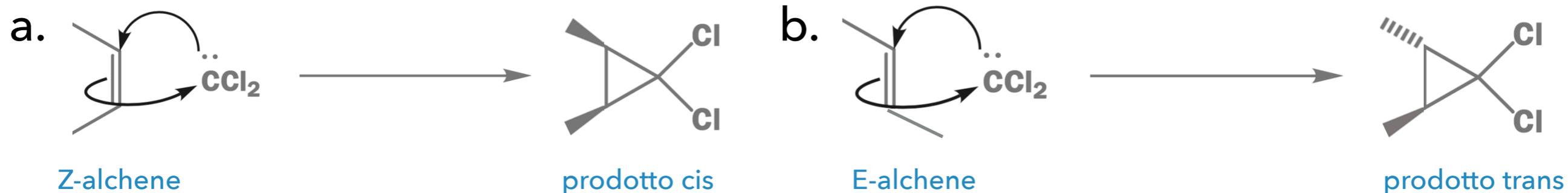


Sintesi di diazocomposti:

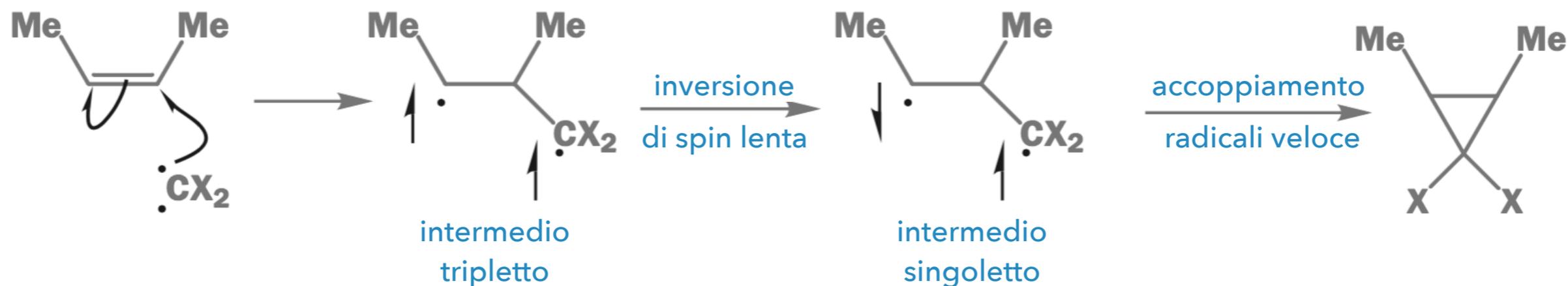


REATTIVITA': REAZIONE CON OLEFINE

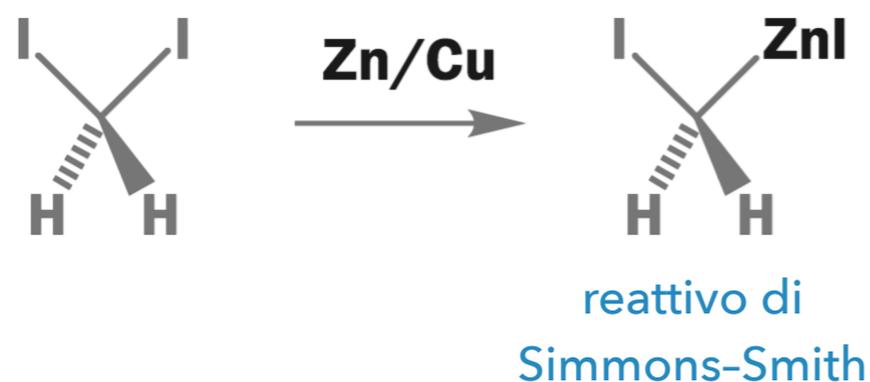
- ▶ Carbene singoletto + olefina: conservazione geometria



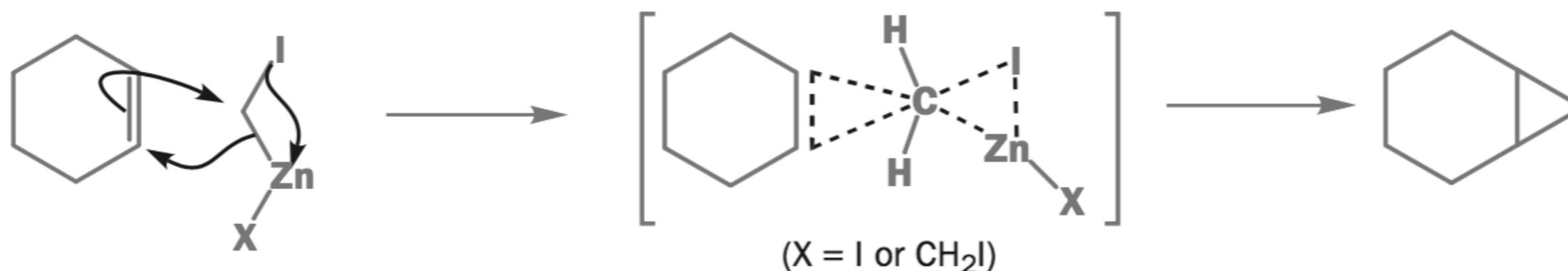
- ▶ Carbene tripletto + olefina: perdita dell'informazione stereochimica



REAZIONE DI SIMMONS–SMITH: CICLOPROPANAZIONE



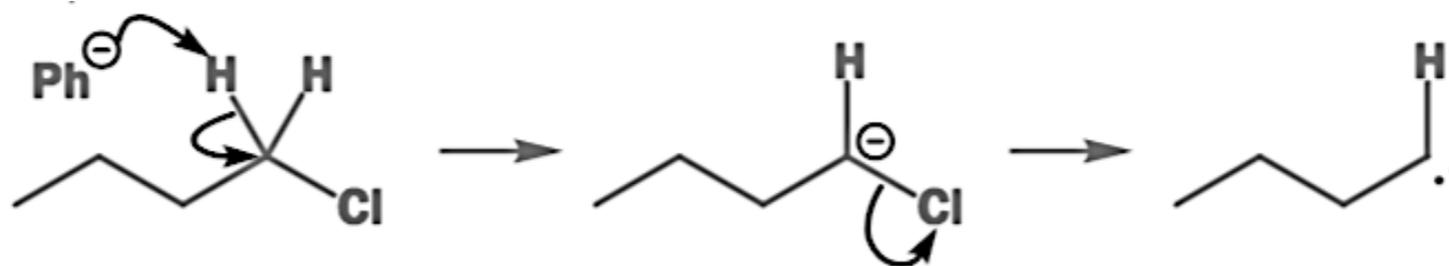
Formazione di carbene in situ (non si utilizza un carbene libero) e trasferimento del carbene sull'olefina.



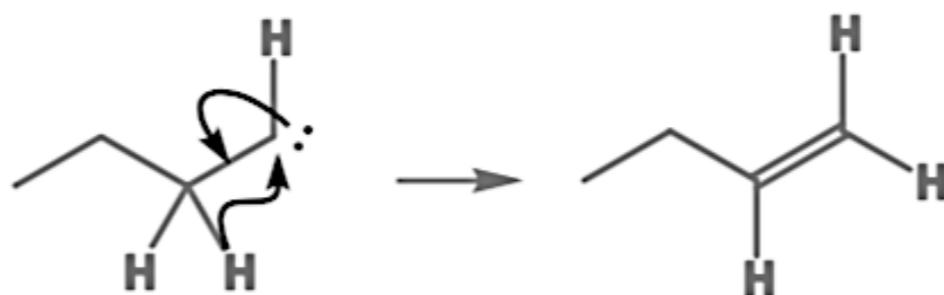
REATTIVITÀ: INSERZIONE NEL LEGAME C-H

- ▶ Migrazione 1,2 di H sul carbene: formazione di alcheni

formazione
del carbene



migrazione 1,2

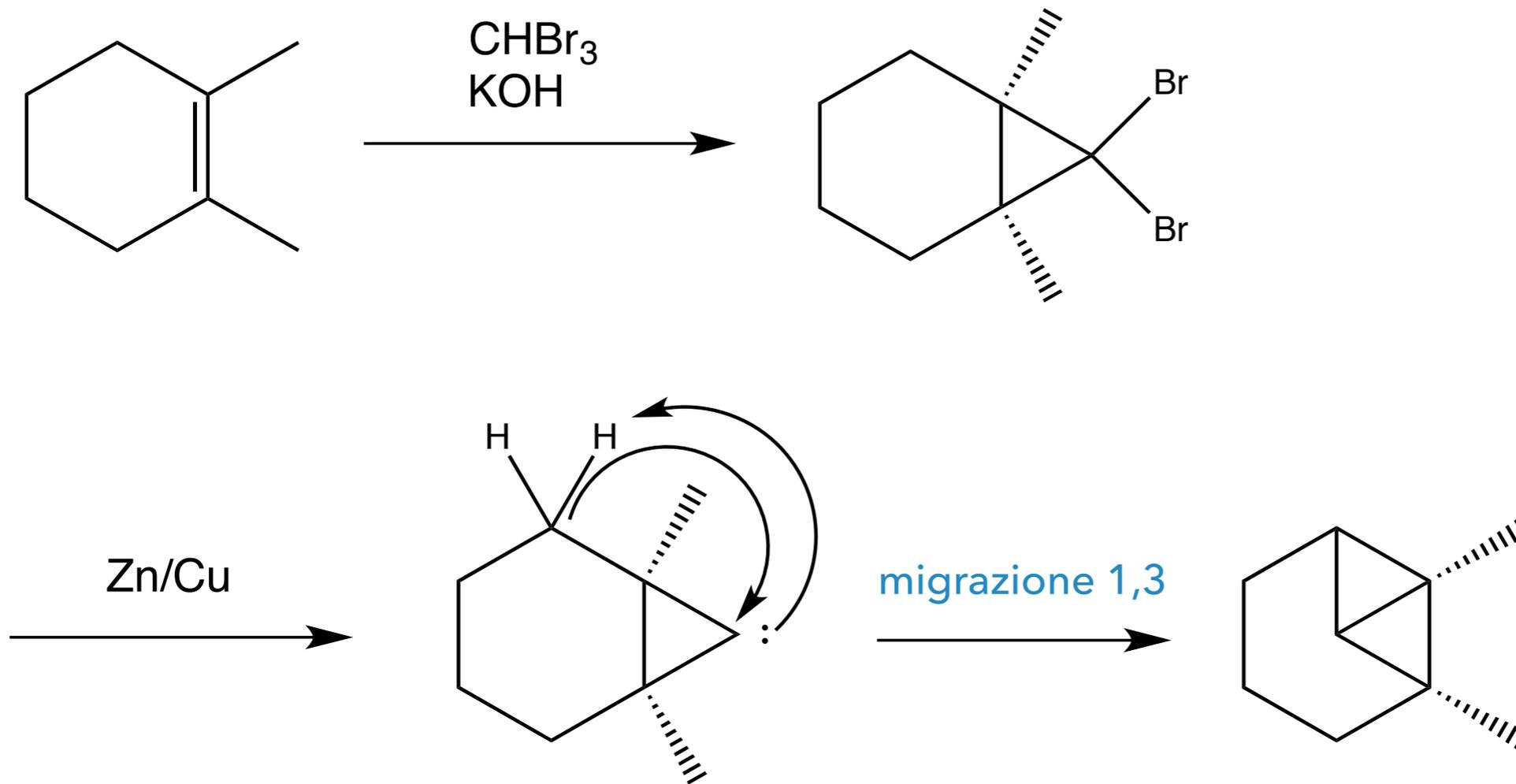


- ▶ Migrazione 1,3: ciclopropanazione intramolecolare



REATTIVITÀ: INSERZIONE NEL LEGAME C-H

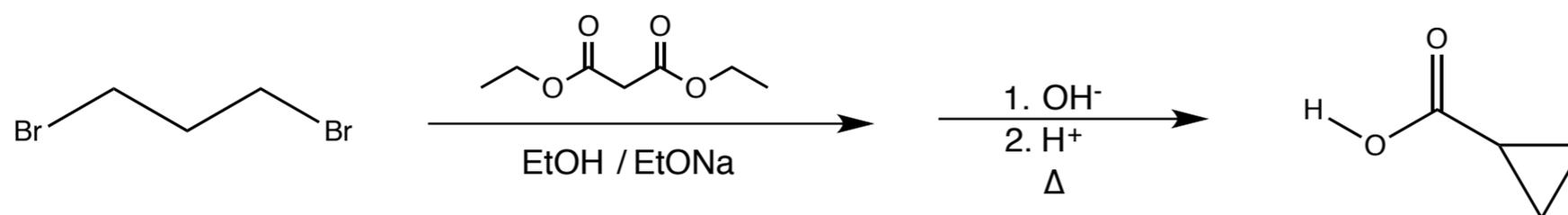
► Migrazione 1,3: esempio



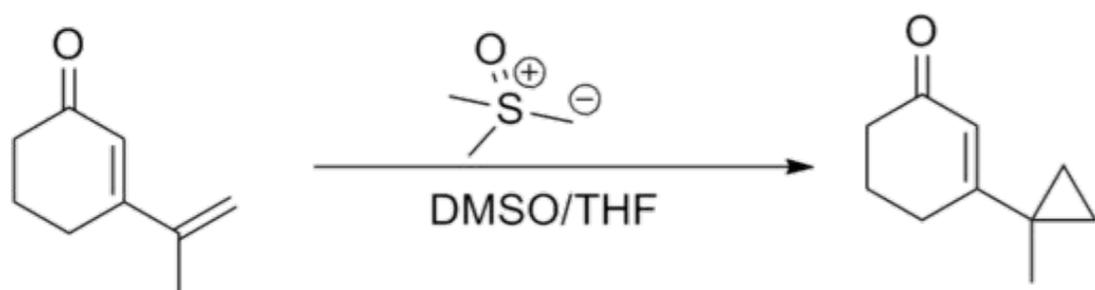
FOCUS: FORMAZIONE DI ANELLI

Anelli a 3:

► sintesi malonica:



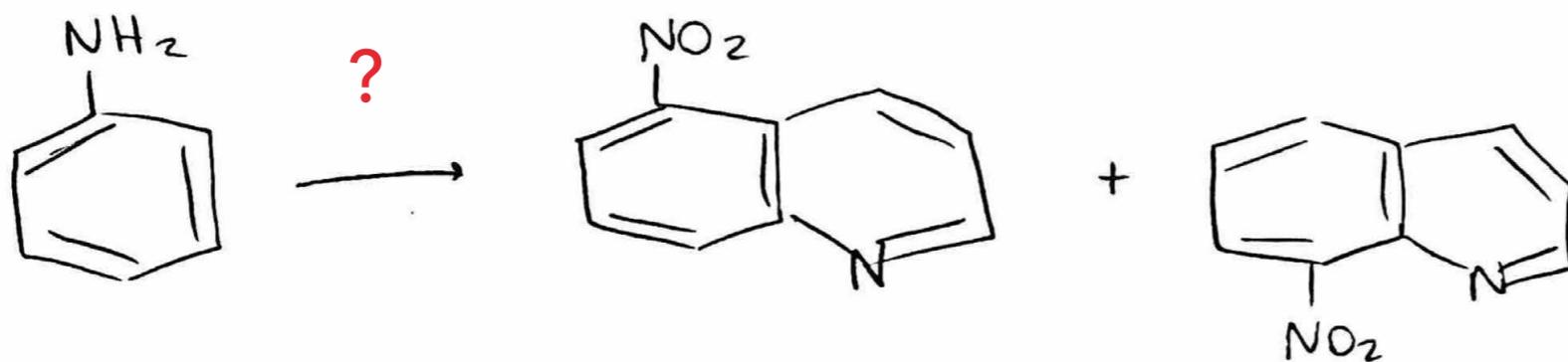
► reazione con ilidi di solfossido (Johnson-Corey-Chaykovsky)



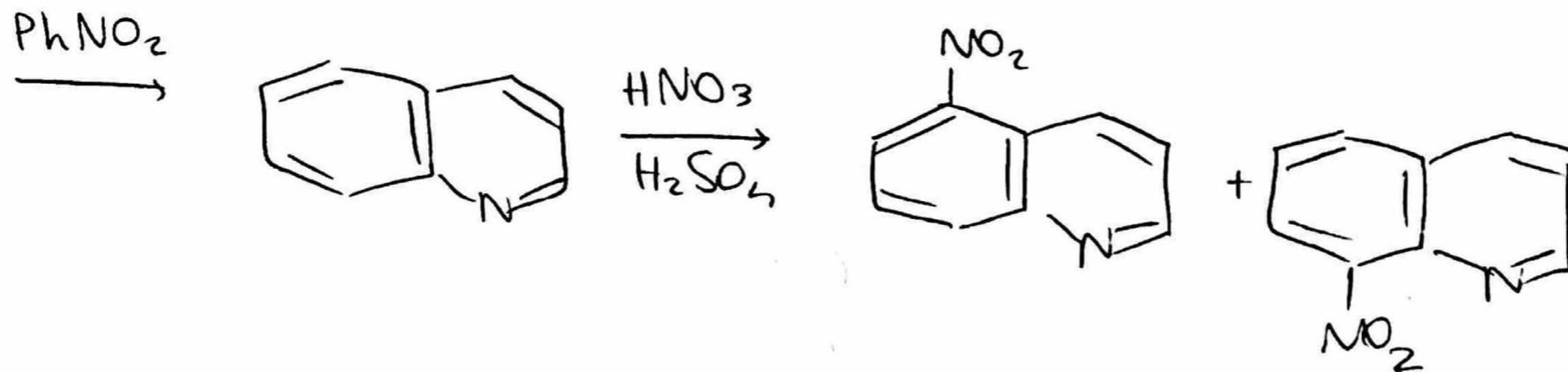
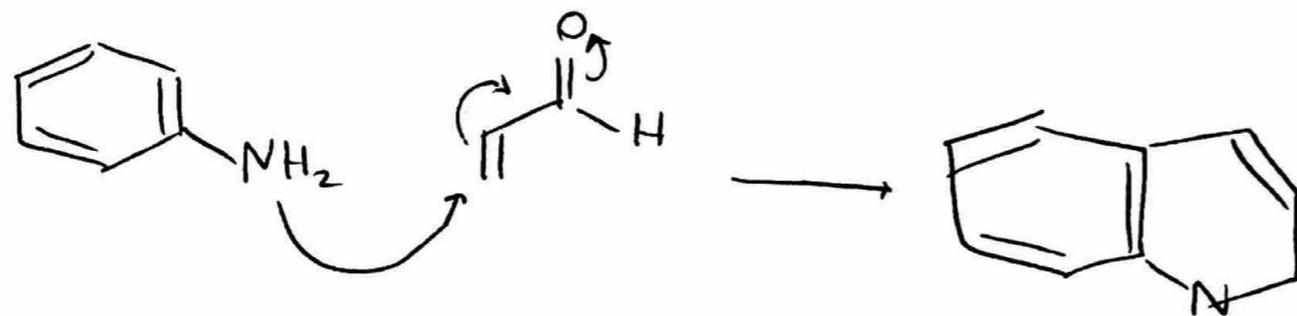
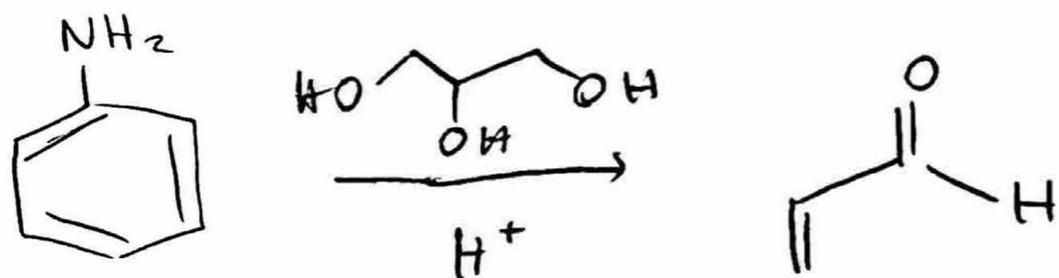
avviene su alcheni
elettronpoveri

su sistemi coniugati

Scrivere i reagenti mancanti ed i passaggi per la seguente trasformazione:

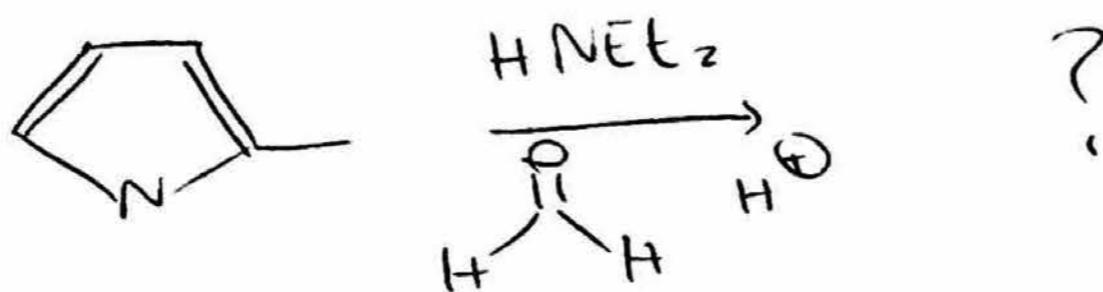


Soluzione:

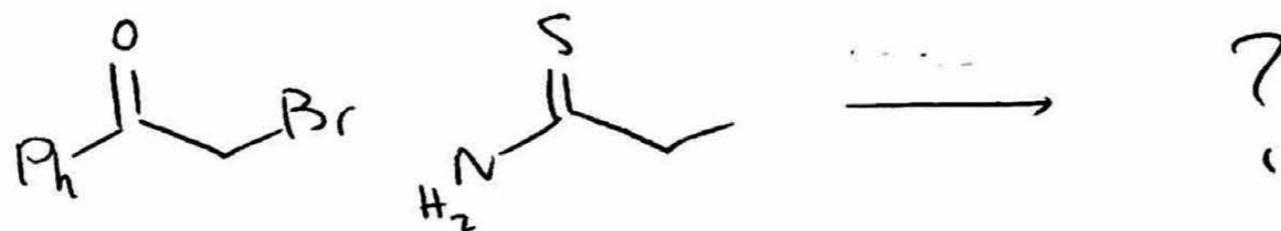


Scrivere il prodotto finale e i passaggi necessari di queste reazioni:

1.

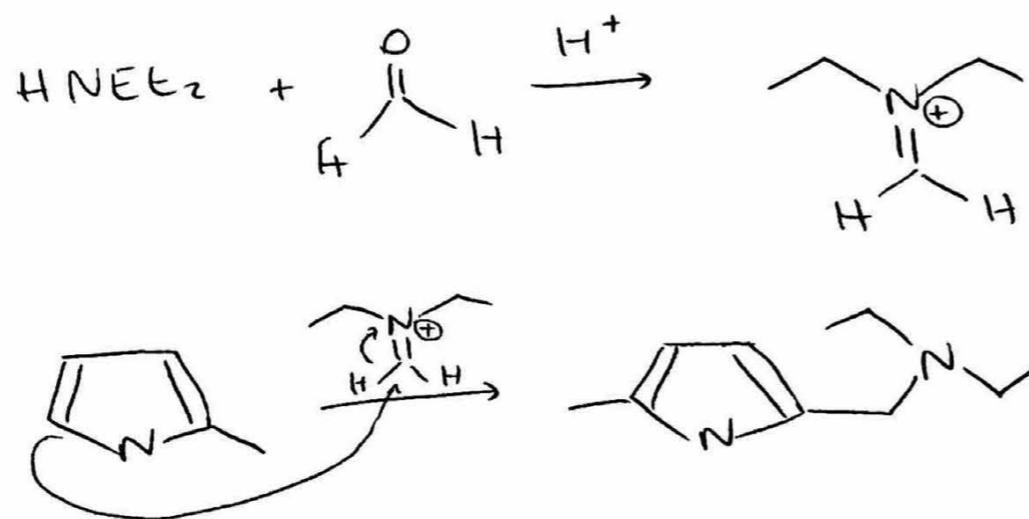


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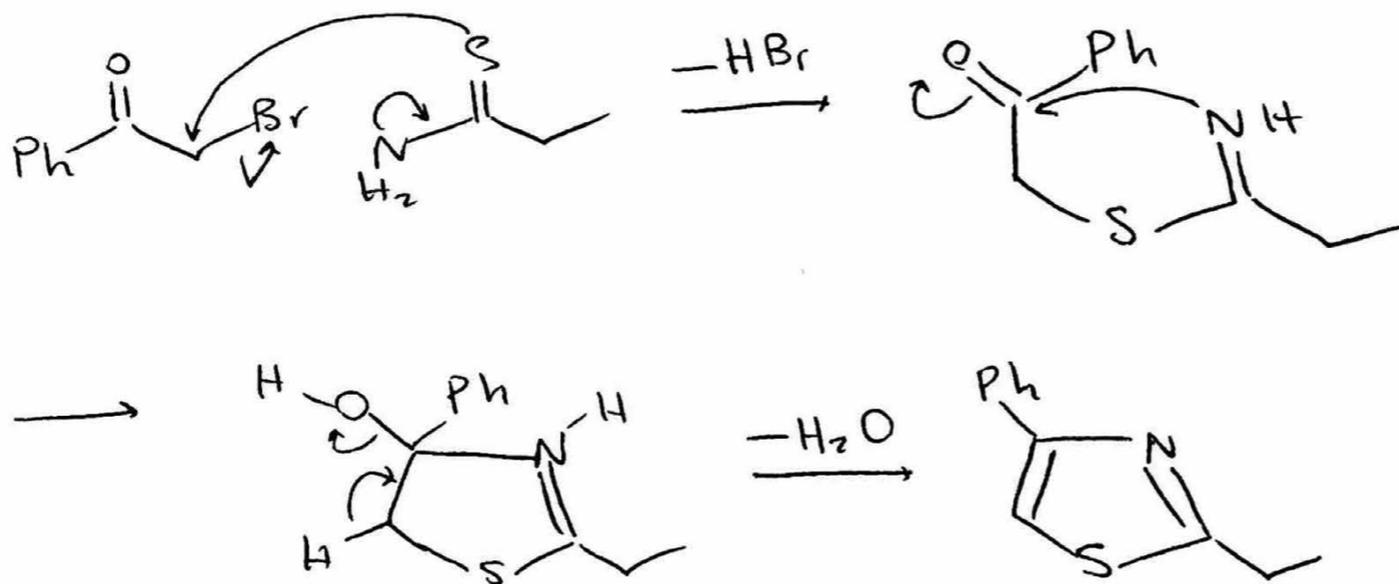


Soluzione:

1.

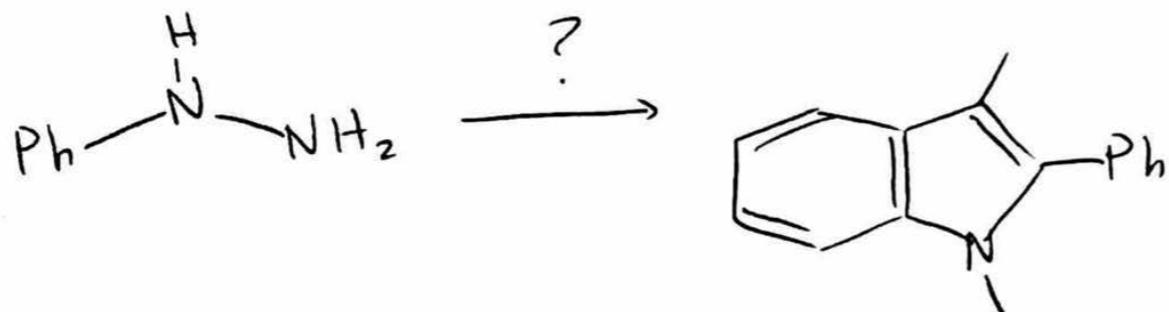


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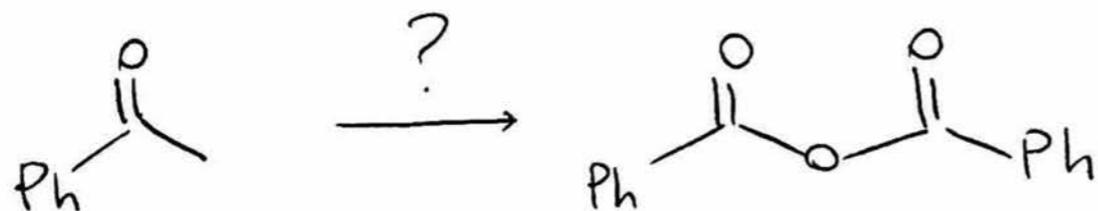


Scrivere i reagenti mancanti ed i passaggi per la seguente trasformazione:

1.

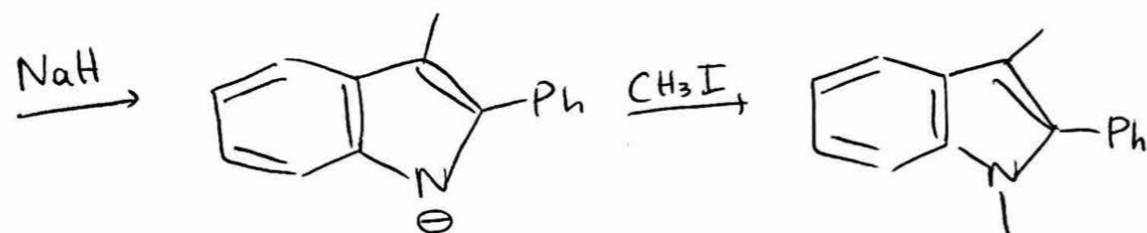
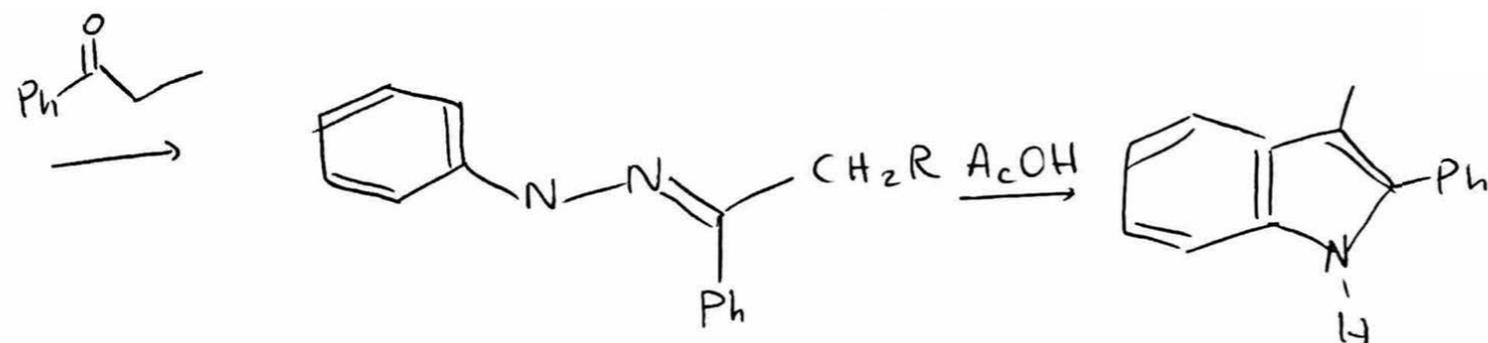


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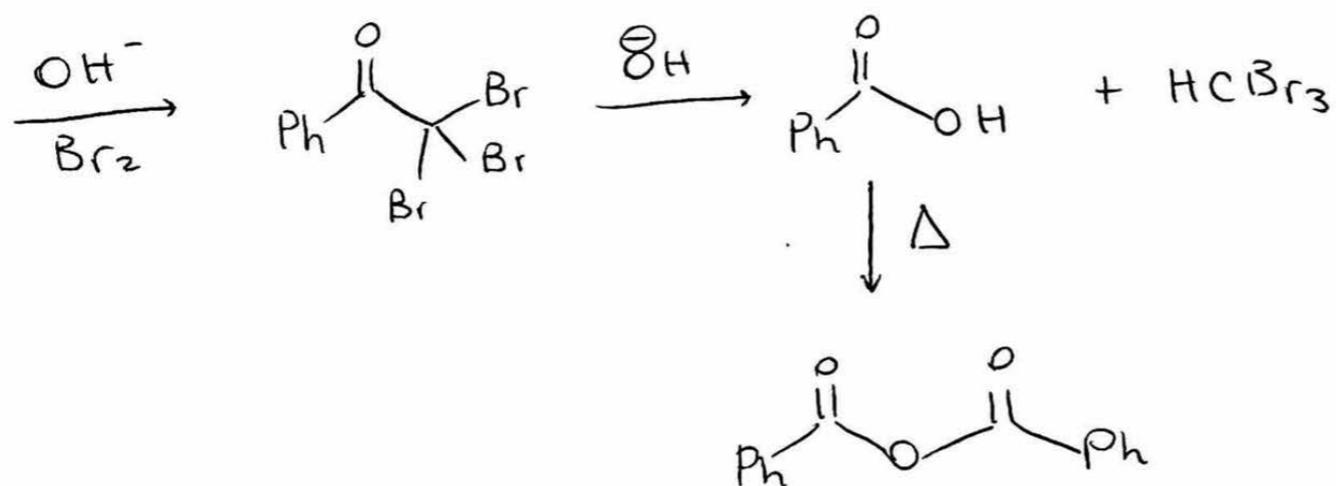


Soluzione:

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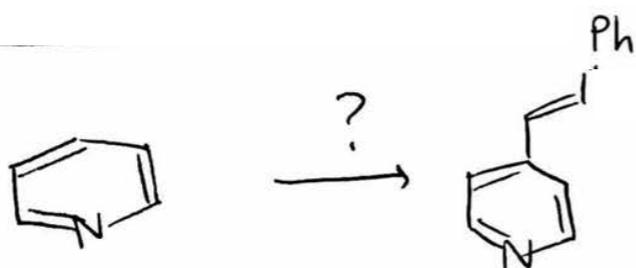


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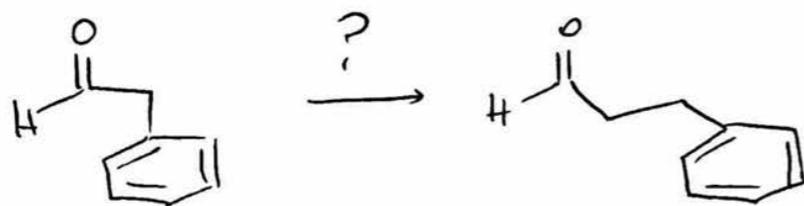


Scrivere i reagenti mancanti ed i passaggi per la seguente trasformazione:

1.

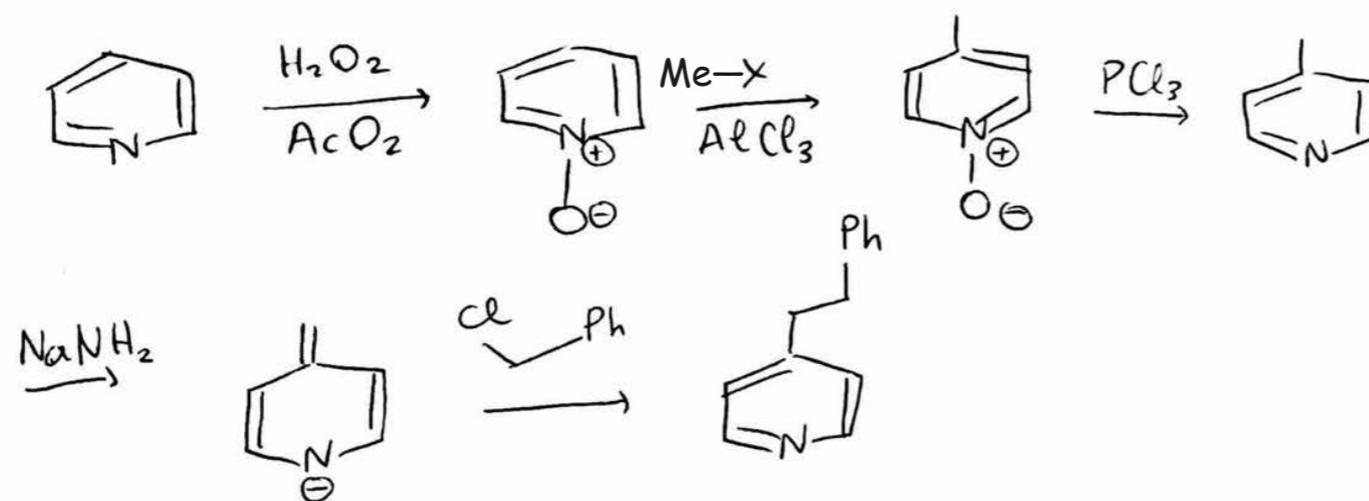


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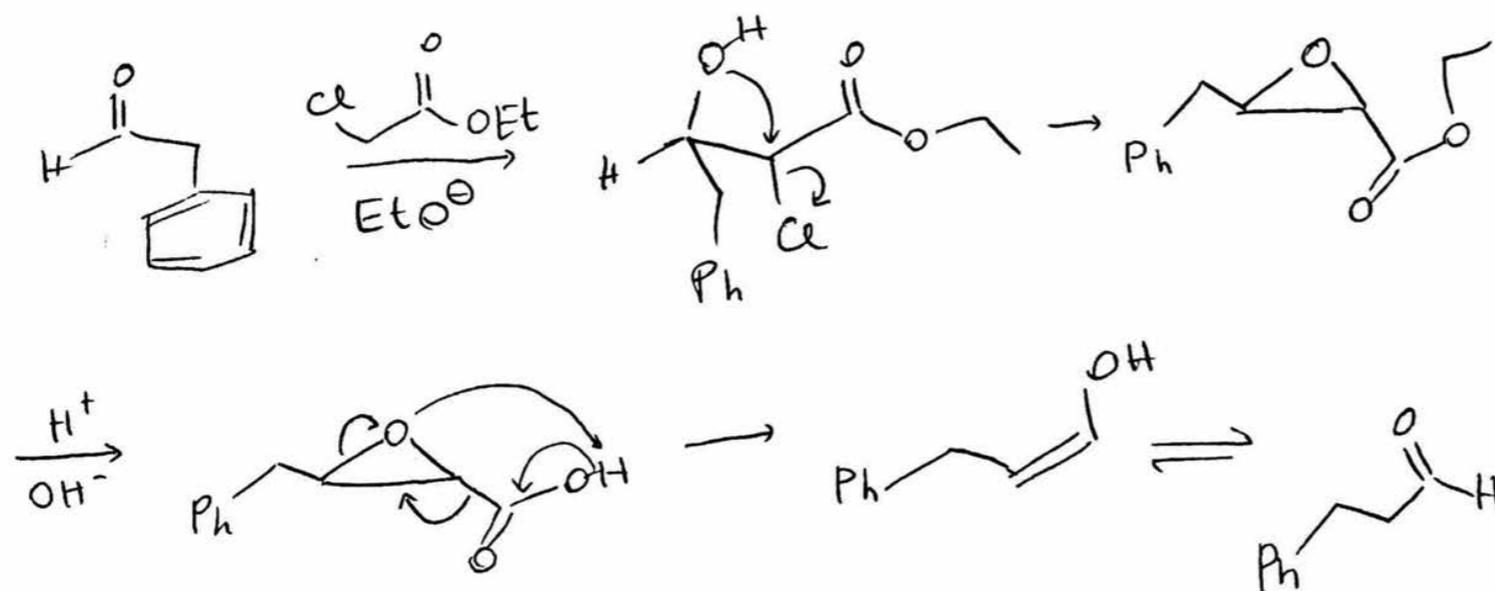


Soluzione:

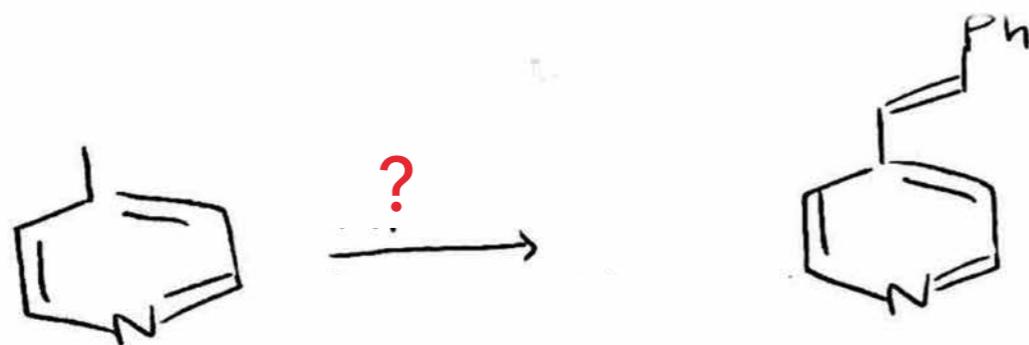
1.



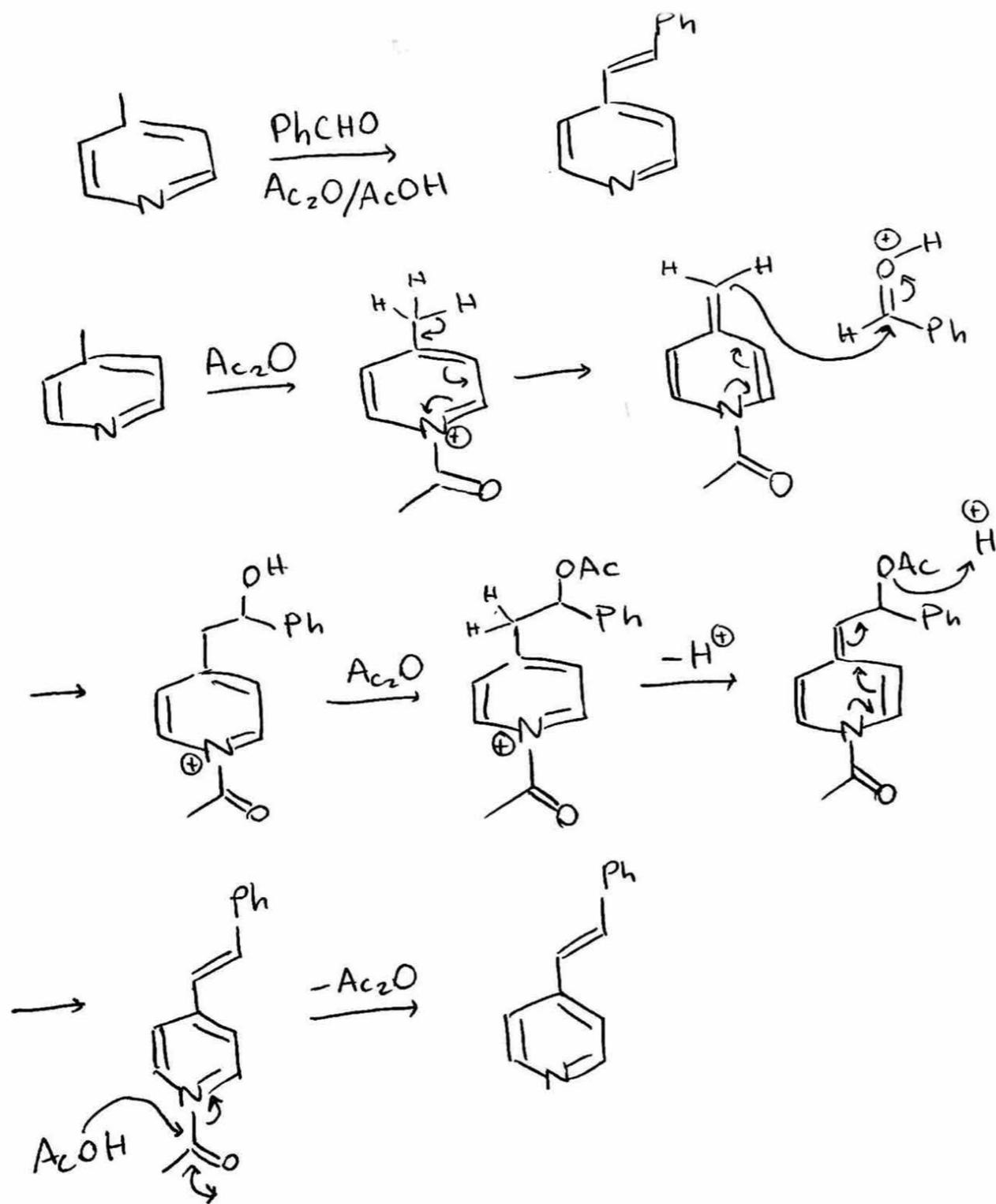
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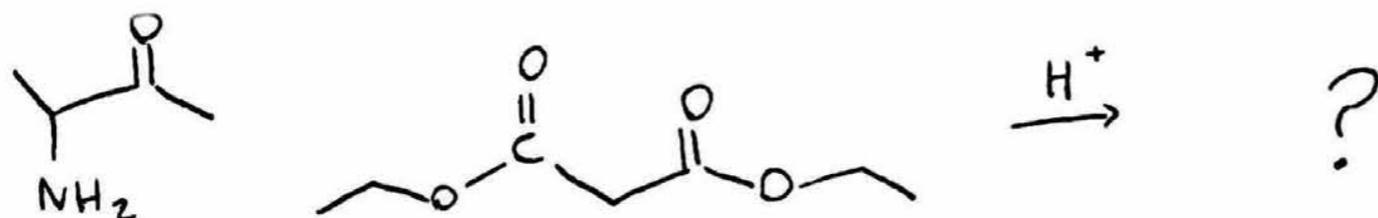
Scrivere i reagenti mancanti ed i passaggi per la seguente trasformazione:



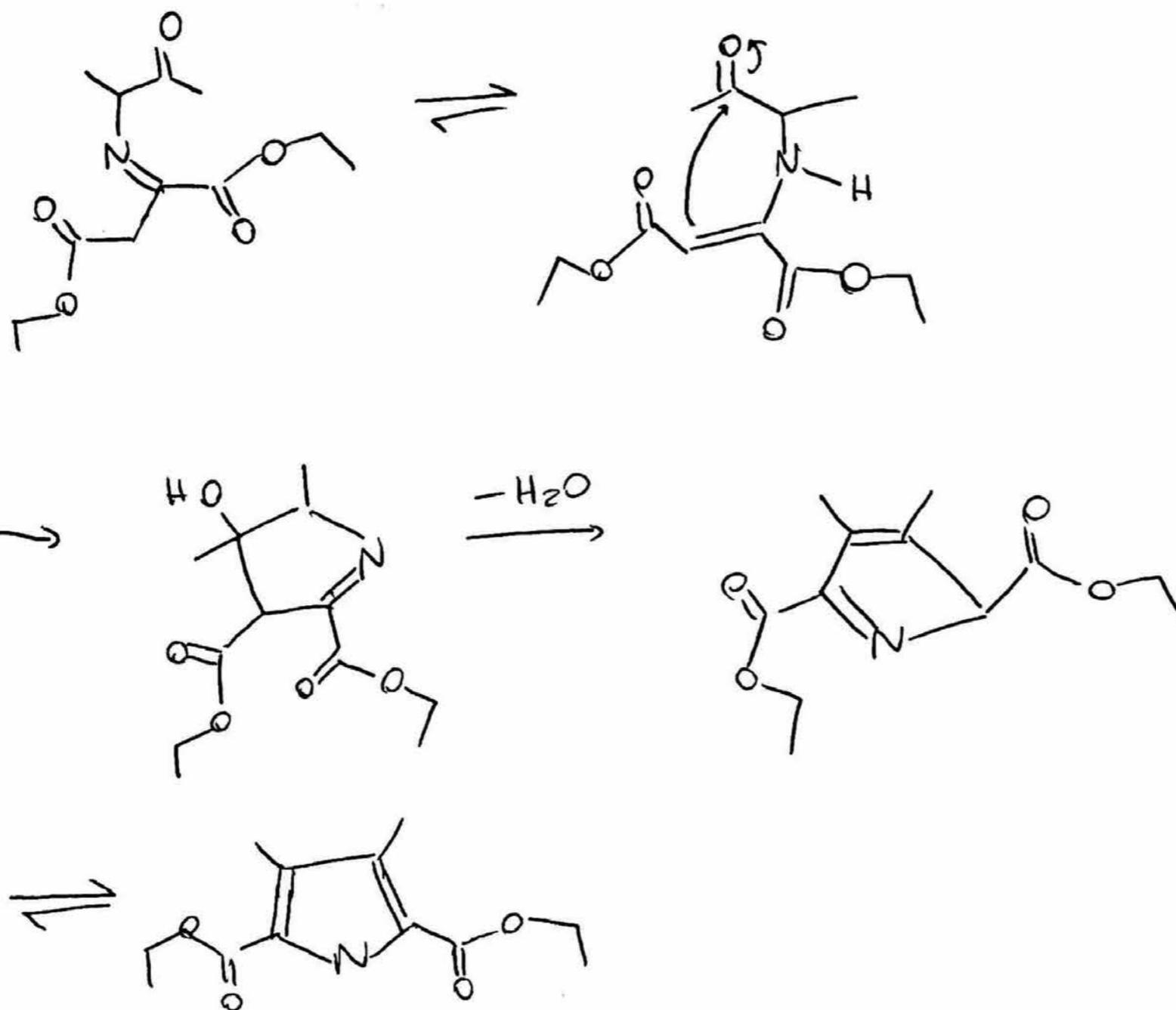
Soluzione:



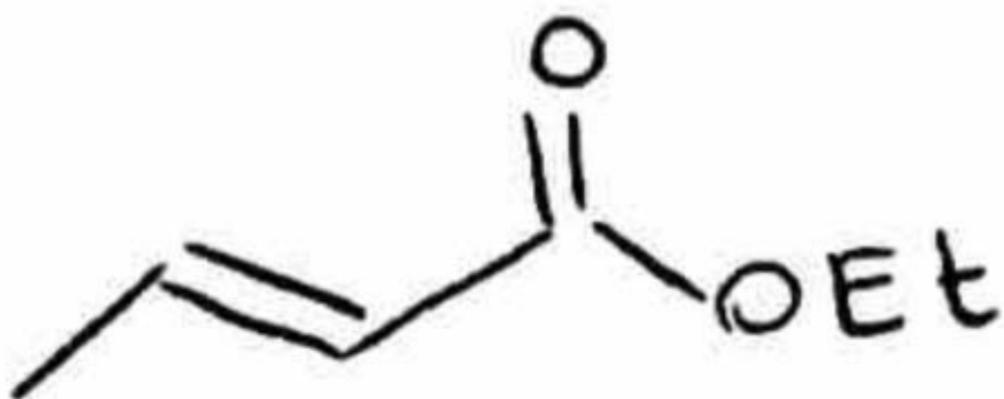
Scrivere il prodotto finale e i passaggi necessari di questa reazione:



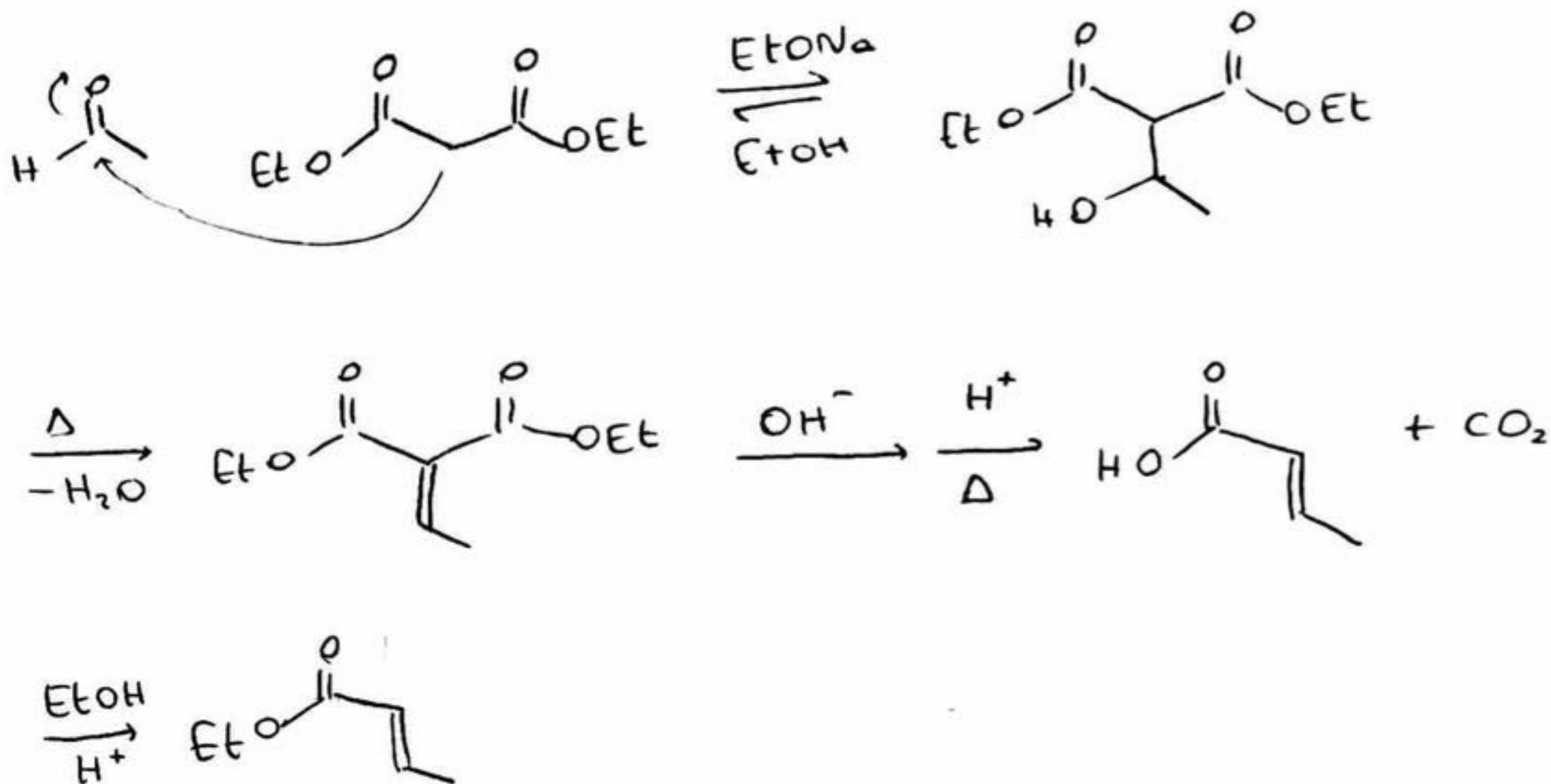
Soluzione:



Sintetizzare il seguente composto:



Soluzione:



β -glucofuranosio e β -glucopiranosio formano un disaccaride tramite legame 1,4 glicosidico. Nel disaccaride il frammento del β -glucofuranosio è non riducente. Scrivere i monosaccaridi e il disaccaride finale.

Soluzione:

