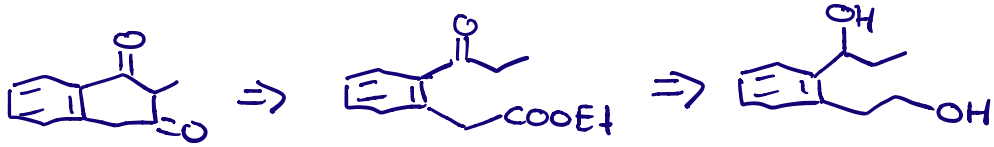
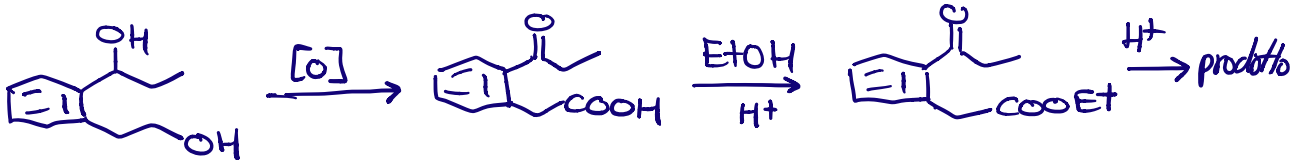
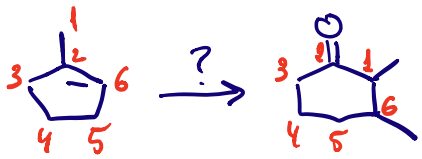
PROBLEMA 1.

(a)

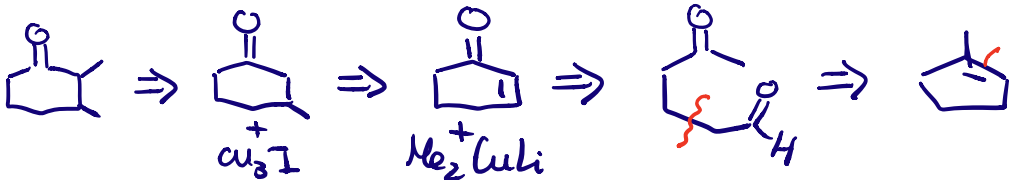
- Le posizioni 1 e 5 sono state ossidate
- Composto 1,3-dicarbonilico ⇒ condensazione chetone + estere.



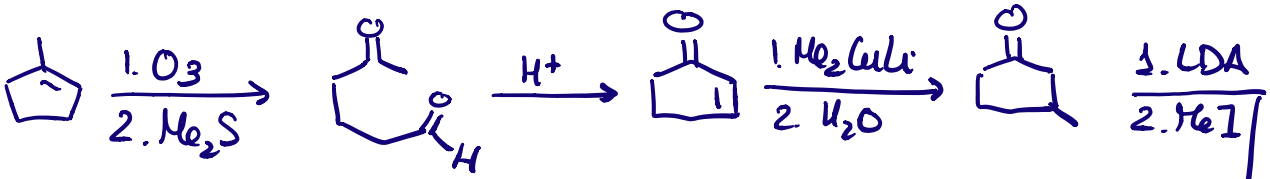
sintesi: 

(b) 

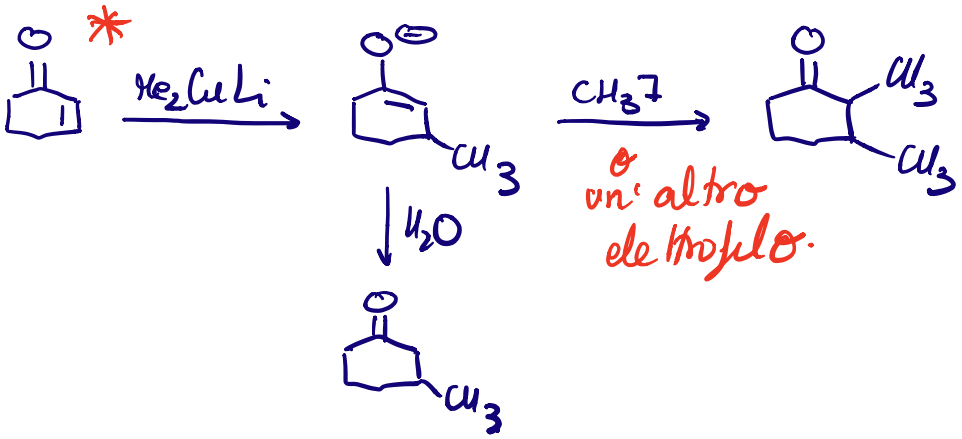
- composto carbonilico α,β-disostituito *
- Il doppio legame posso ossidarlo con O_3



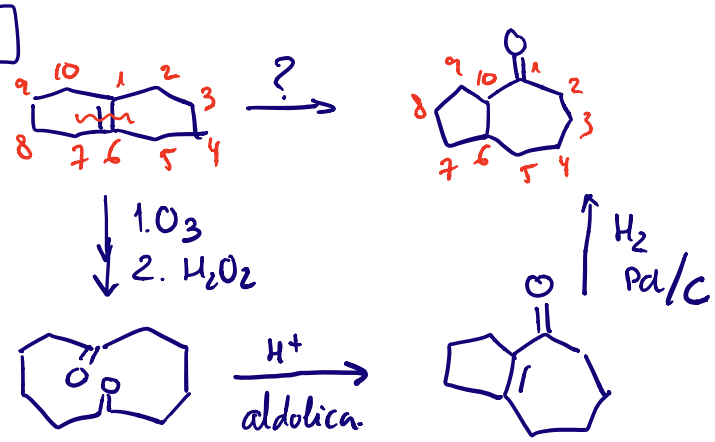
alchilazione in α — addizione 1,4 — condensazione aldolica

sintesi: 

Per evitare la formazione dei due prodotti meglio fare così

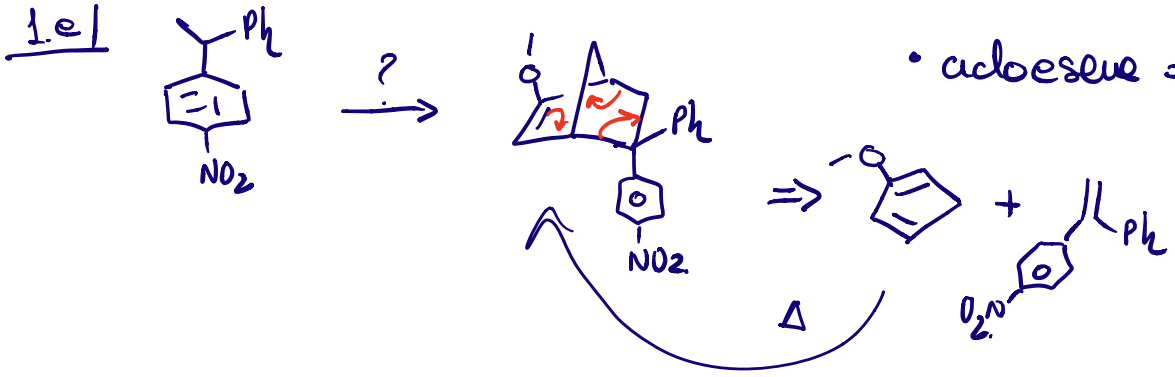


1.c.



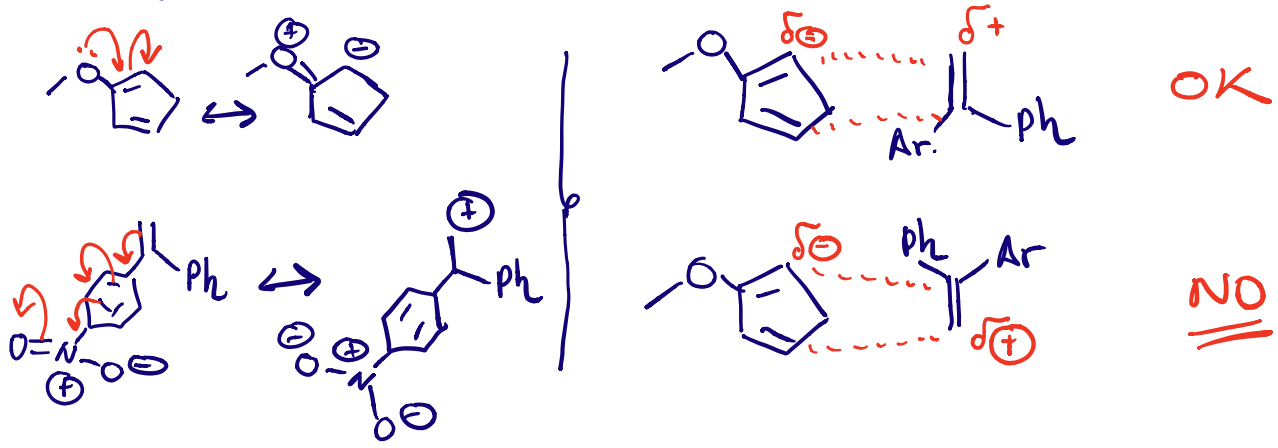
- Le posizioni 1,6 corrispondono al doppio legame che posso ossidare con O_3

1.e

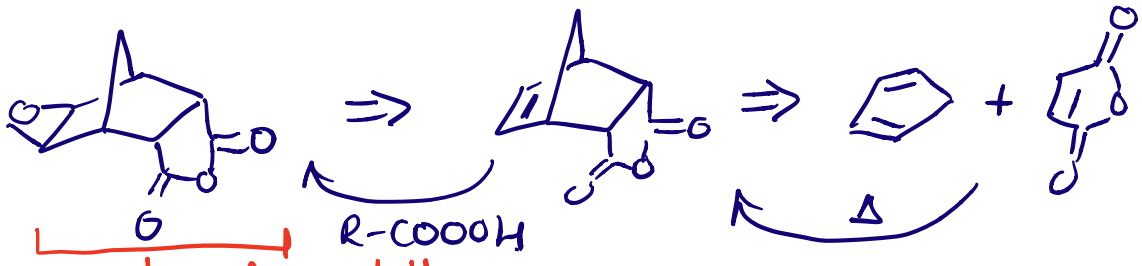


- cicloesene ⇒ Diels-Alder.

Regioselettività:



PROBLEMA 2

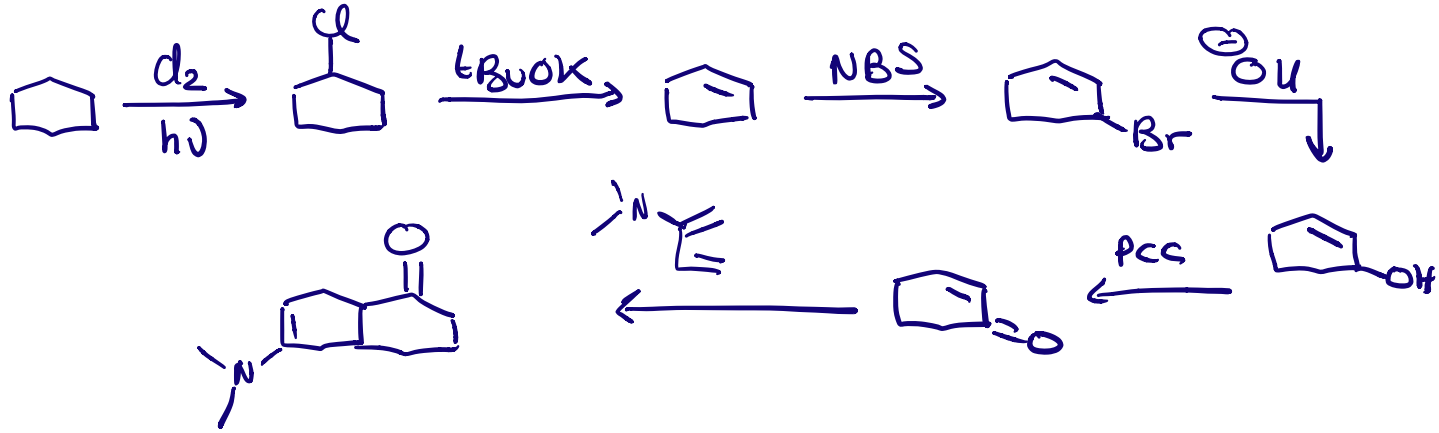


O ricorda al prodotto Diels-Alder

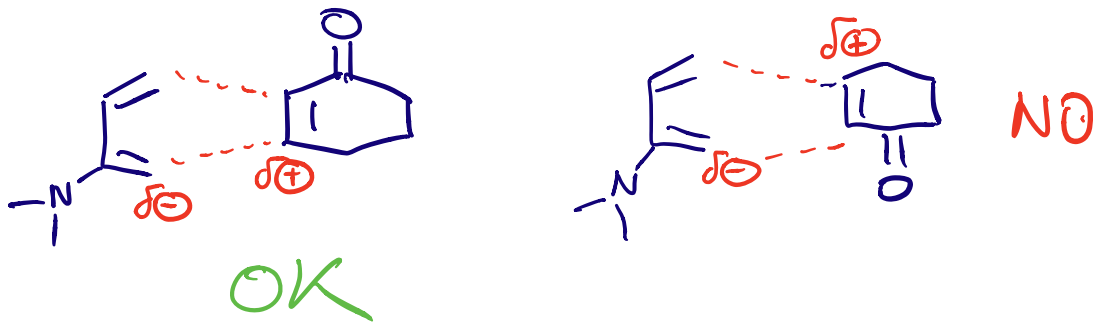
Sintesi. Devo epossidare un doppio legame isolato, ricco in elettroni ⇒ utilizzo peracido come MCPBA. Non posso utilizzare $H_2O_2/OH^{\ominus}$ poichè $HO\text{-}O^{\ominus}$ è anche esso ricco di elettroni

PROBLEMA 3

a)



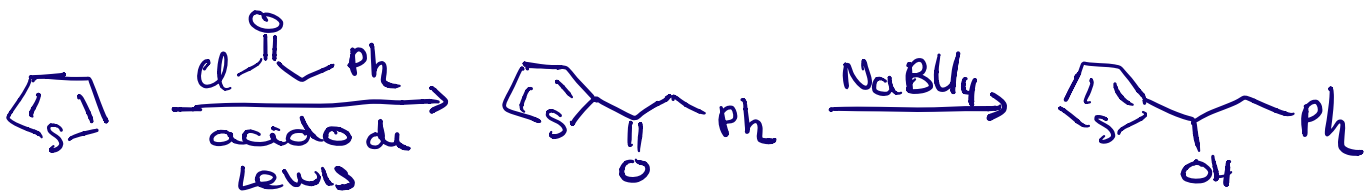
Regioselettività Diels-Alder.

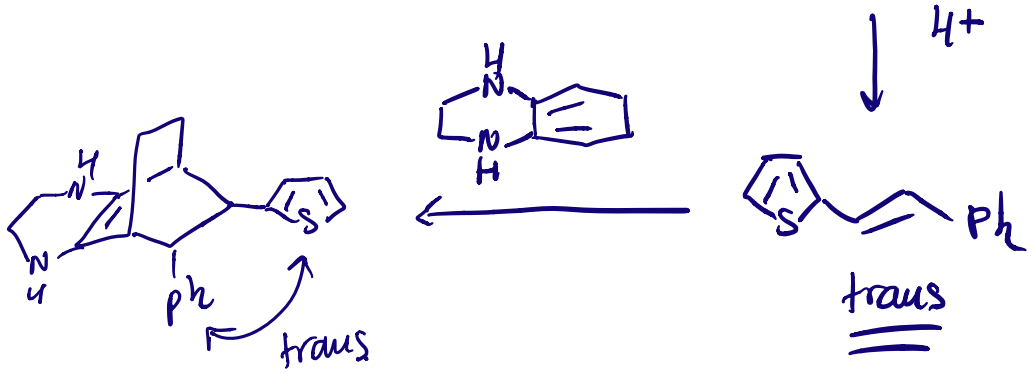


OK

NO

b)





INCOGNITO $C_{10}H_{13}NO_2$

U = 5 ; aromatico (4) + altro

$\bar{\nu}$	assegnazione	conferma
1740 cm^{-1}	$\nu_{C=O}$	estere non coniugato	segnale 170 ppm al ^{13}C-NMR
3100 cm^{-1} >	ν_{NH}	NH o NH_2	singoletto largo per 2H 8.90 ppm
1600, 1500	$\nu_{C=C}$	aromatico	^1H, ^{13}C-NMR.

$-\overset{O}{\overset{\|}{C}}-O-$ $-NH_2$ mancano 3C

^1H-NMR

- Vedo 5H aromatici ⇒ benzene monosostituito
  - → Mancano ancora 6H
  - → Zona alifatica 3 segnali >3 ppm. deschermati
    - dd, 1H, CH legato a $-CH_2-$
    - s, 3H,
    - sistema AB, dd + dd, J = 14 Hz, 7.6 Hz., 2H, tipico di CH_2 vicino a centro chirale (il CH)

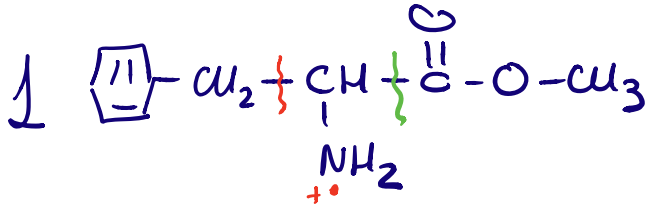
$-NH_2$ $-\overset{O}{\overset{\|}{C}}-O-$ $-CH_2-\underset{1}{CH}-$ $-CH_3$

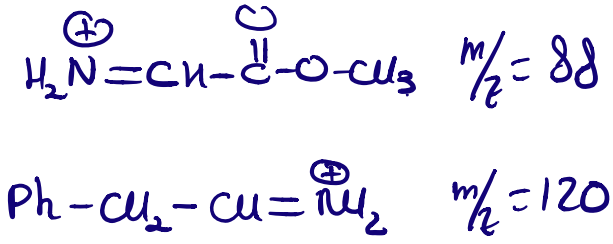
δ ppm. CH > CH_3 > CH_2 ⇒ sicuramente CH, CH_3 vicini a eteroatomo. Vado al ^{13}C-NMR. Nella parte alifatica vedo

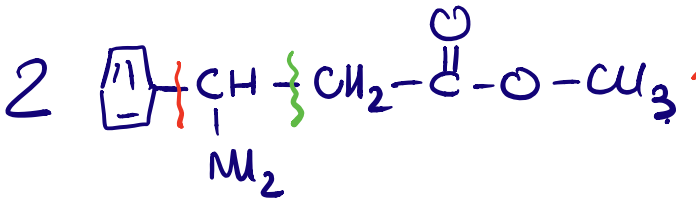
≈50 ppm CH, CH_3 → legate a eteroatomo

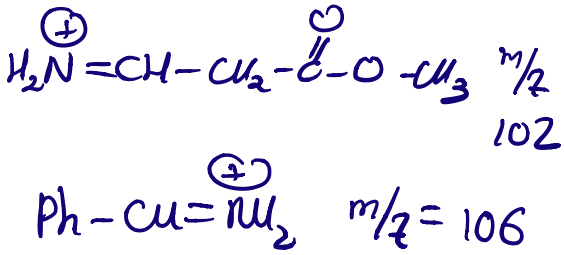
~35 ppm CH_2 → deschermato ma non legato a eteroatomo.

Due possibilità

1 



2 



MS → corrisponde alla molecola 1

$C_7H_5NO_3$ $U = 6$ aromatico + 2

IR

$\nu_{C=O}$ ~ 1700 cm^{-1} + $\nu_{C=O}$ 2764 cm^{-1} / ν_{H} 2868 cm^{-1}	aldeide aldeide	conferma: ^1H-NMR: singoletto 10 ppm. ^{13}C-NMR: segnale a 190 ppm.

Vedo altre due segnali forti a 1550 e 1370 cm^{-1} $\Rightarrow$ NO_2 $\Rightarrow$ conferma presenza picco $M-NO_2$ nello spettro di massa. $m/z = 105$.

Alla massa vedo anche $M-1$ confermando la presenza di aldeide

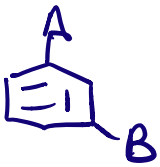
$-C(=O)-H$ $-NO_2$

ho già tutto $\Rightarrow$ aromatico disostituito

vado a ^1H e ^{13}C

^1H: d, 2H + d, 2H

^{13}C: 4 segnali



^1H: s(1H) + d(1H) + dd(1H) + d(1H)

^{13}C: 6 segnali

^1H: d(1H) d(1H) dd(1H) dd(1H)

^{13}C. 6 segnali

^1H-NMR vedo lo che corrisponde a meta-disostituito