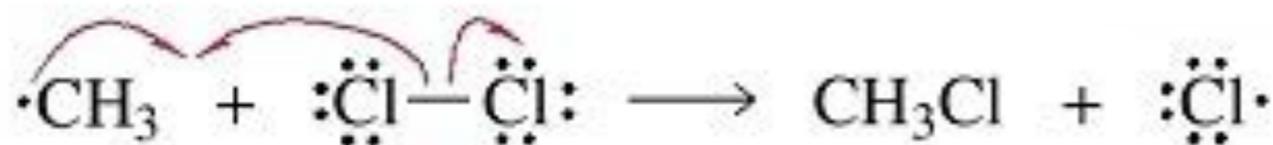
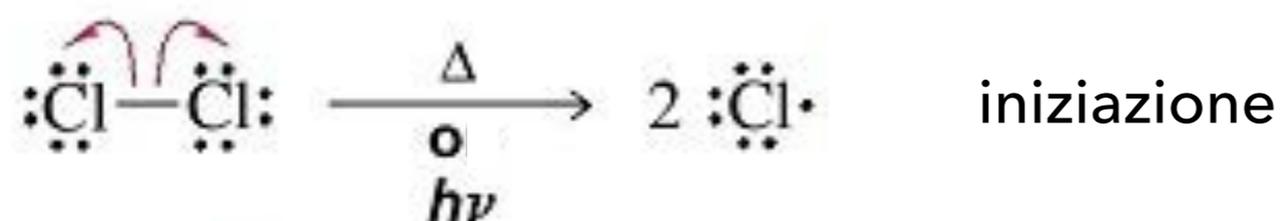


▶ **RADICALI**

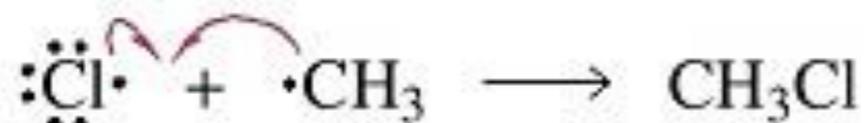
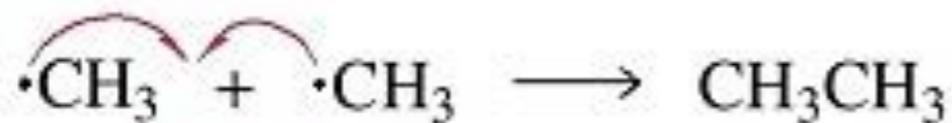
LEZIONE 3

RADICALI: REAZIONI A CATENA

Alogenazione alcani



propagazione



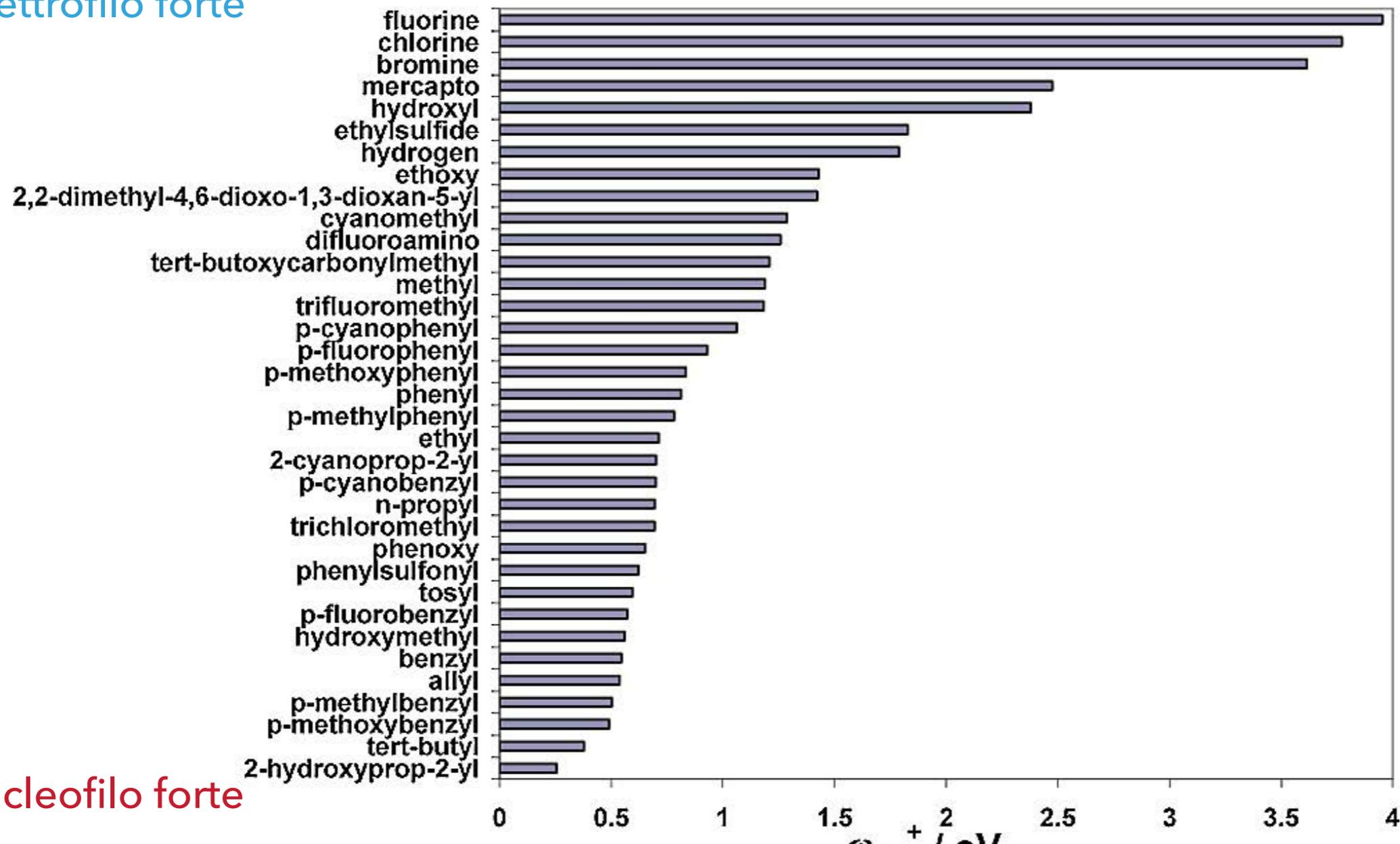
terminazione

RADICALI ELETTROFILI E NUCLEOFILI

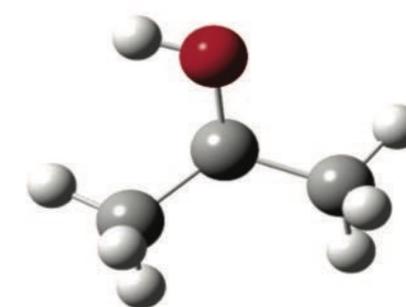
Radicale localizzato su SOMO di:

- ▶ atomo elettronegativo \Rightarrow radicale elettrofilo
- ▶ atomo poco elettronegativo \Rightarrow radicale nucleofilo

elettrofilo forte



fluoro radicale

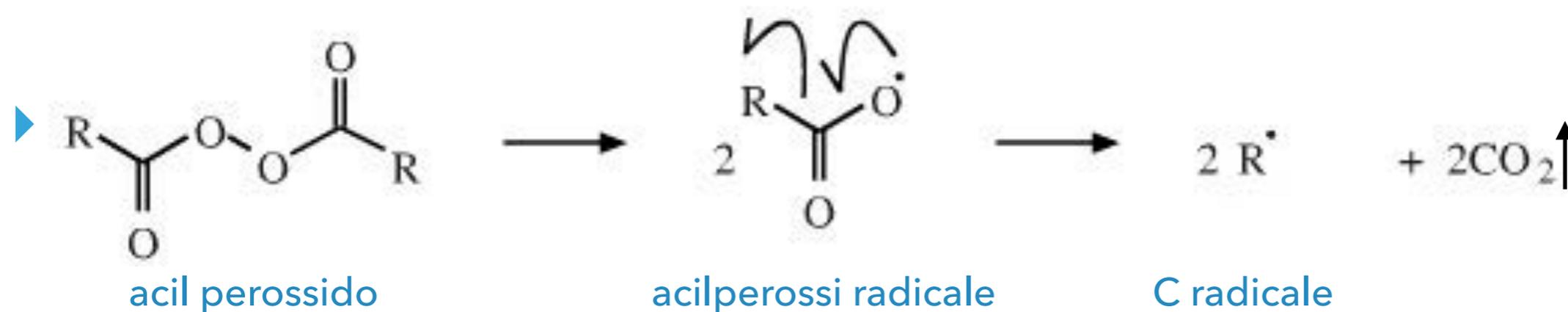
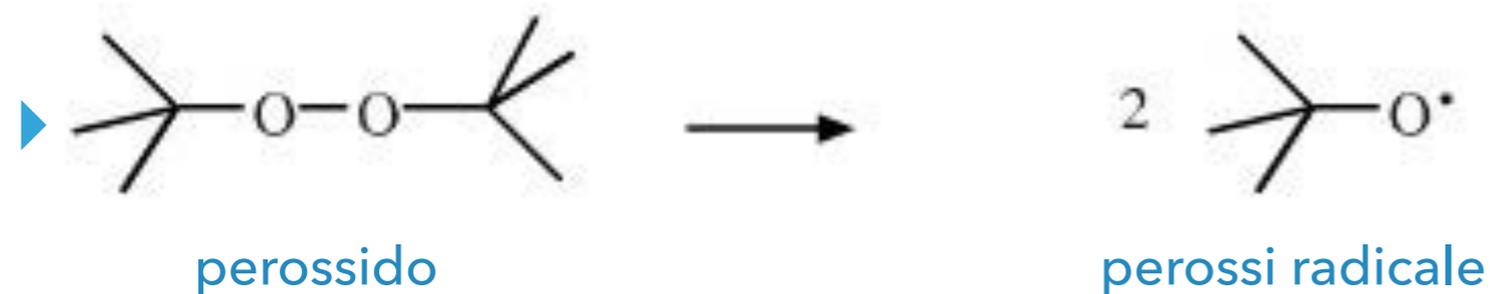


2-idrossiprop-2-il radicale

nucleofilo forte

FORMAZIONE DI RADICALI

Iniziazione:



FORMAZIONE DI RADICALI

Propagazione:

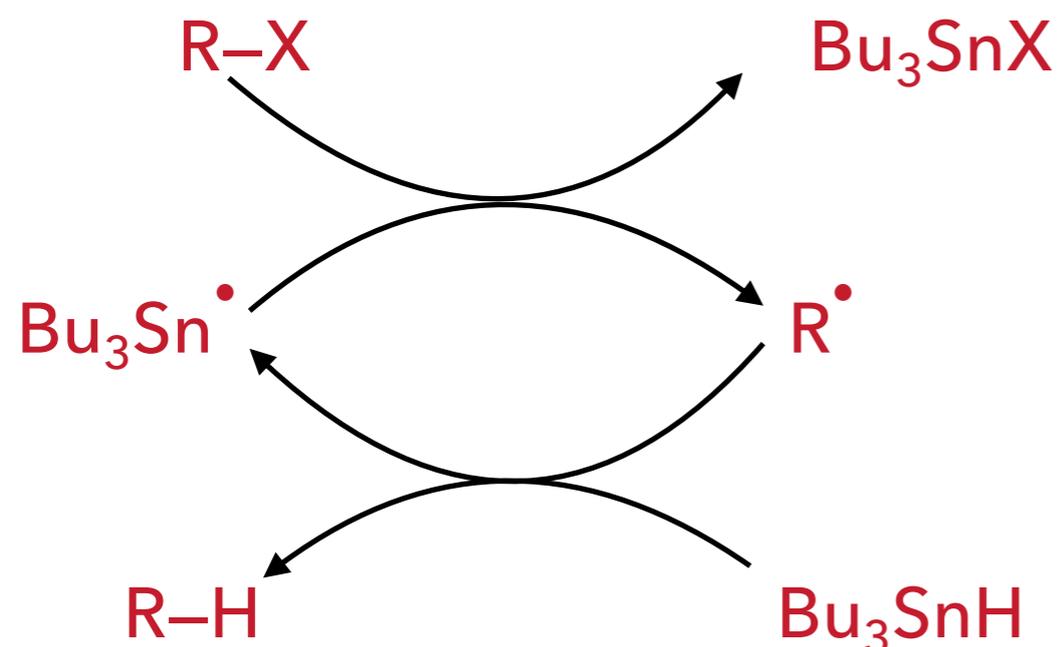
- ▶ Se $E_{(X-Z)} \gg E_{(R-X)}$ (condizione difficile da ottenere):



- ▶ utilizzo di intermedio radicale facilmente generabile:

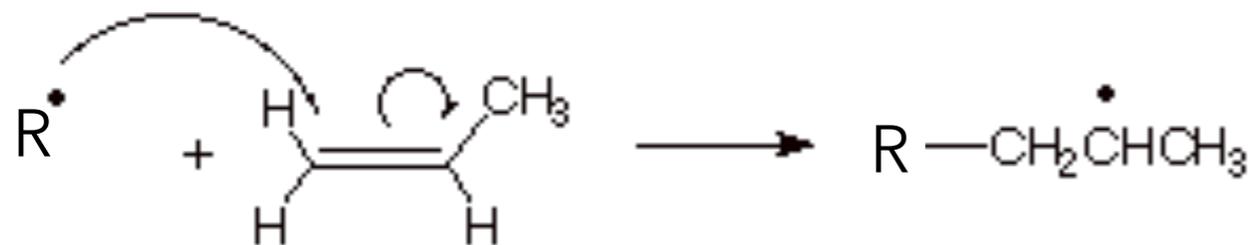


- ▶ Riduzione radicalica di alogenuri alchilici ad alcani:



ADDIZIONE DI RADICALE AD ALCHENE

- ▶ Addizione all'alchene: NO!

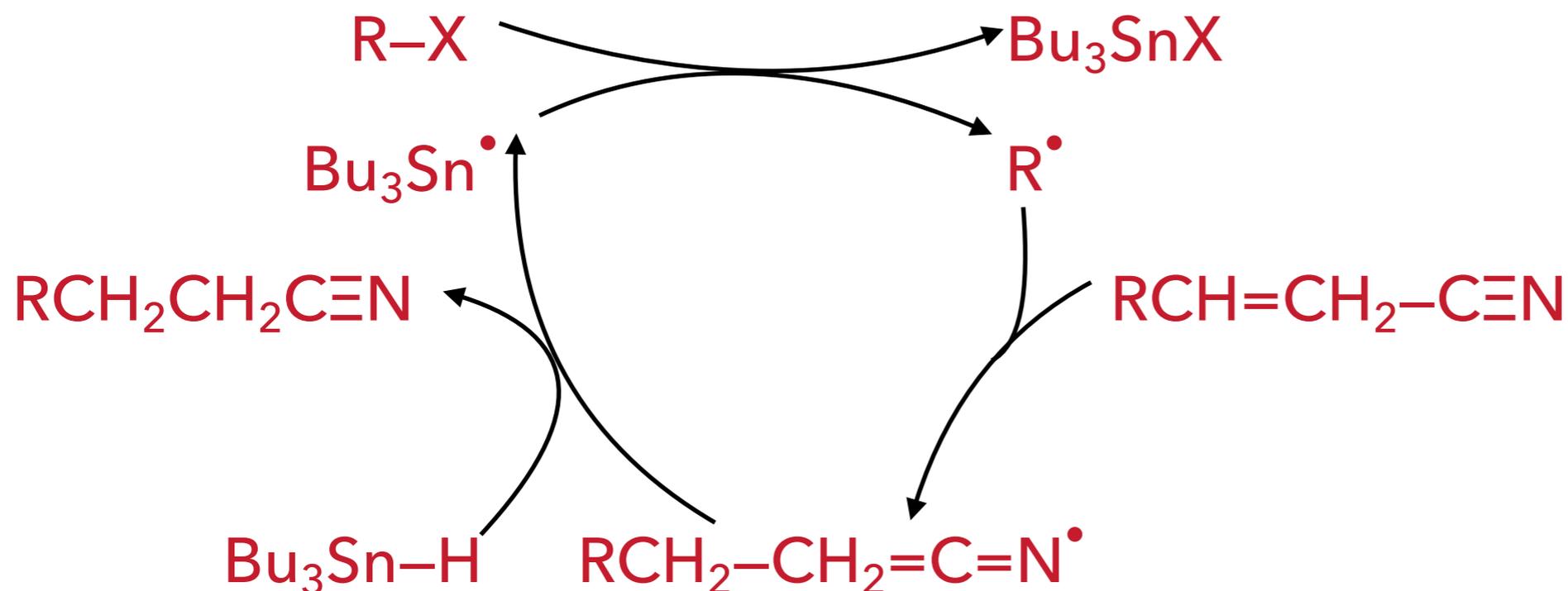


C radicale
nucleofilo

alchene
nucleofilo

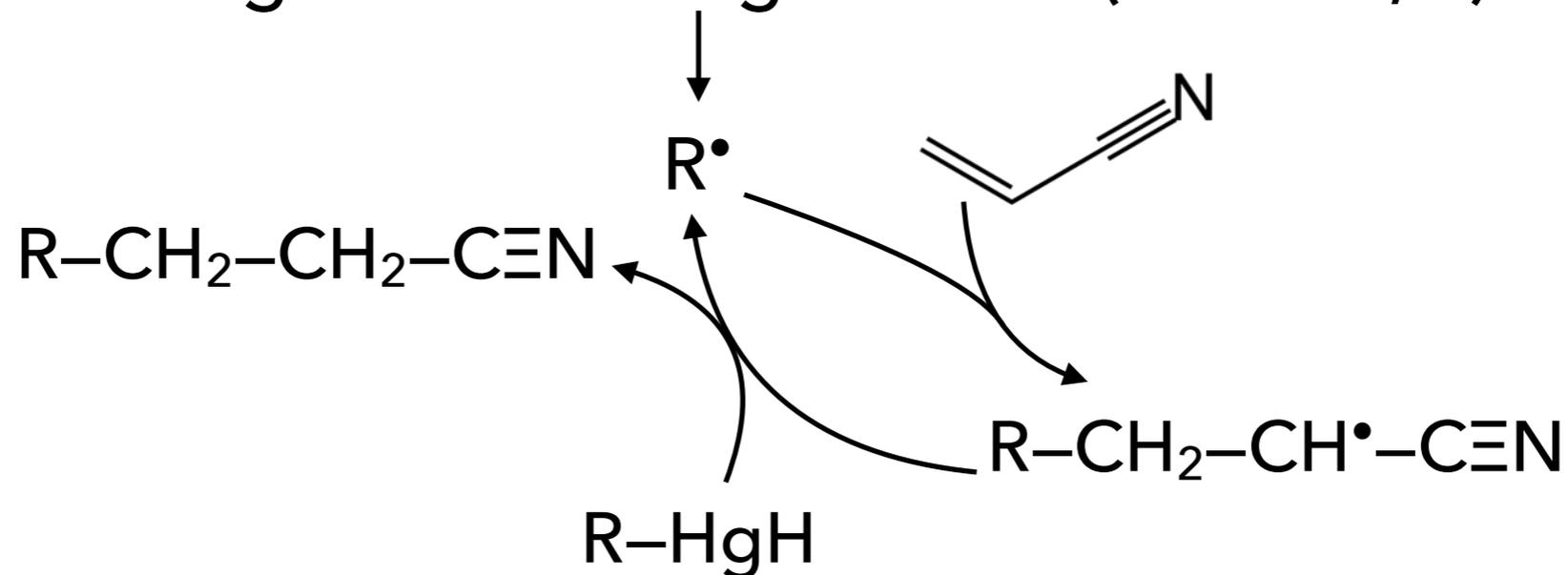
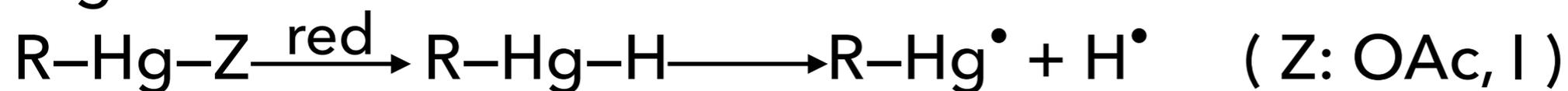
⇒ la reazione NON avviene

- ▶ Addizione coniugata:

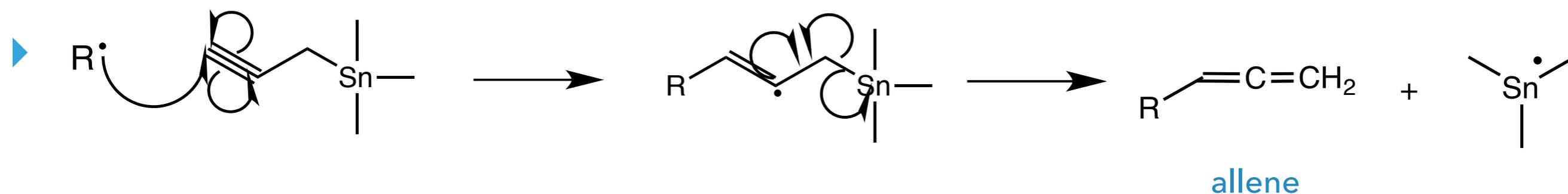
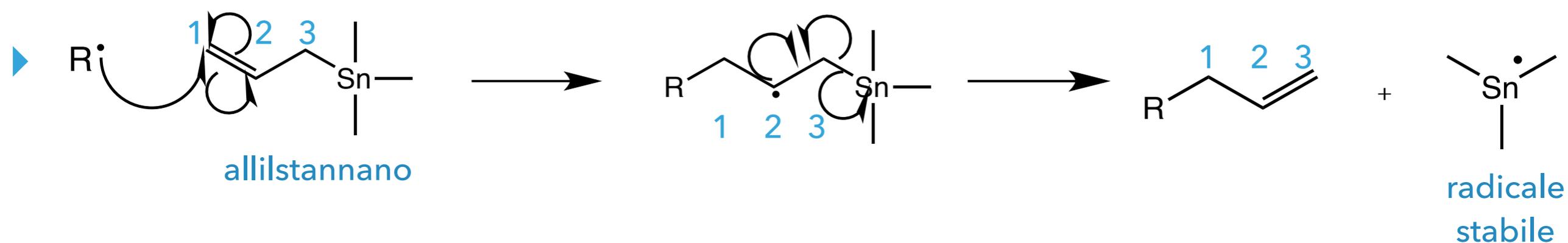


ADDIZIONE DI RADICALE AD ALCHENE

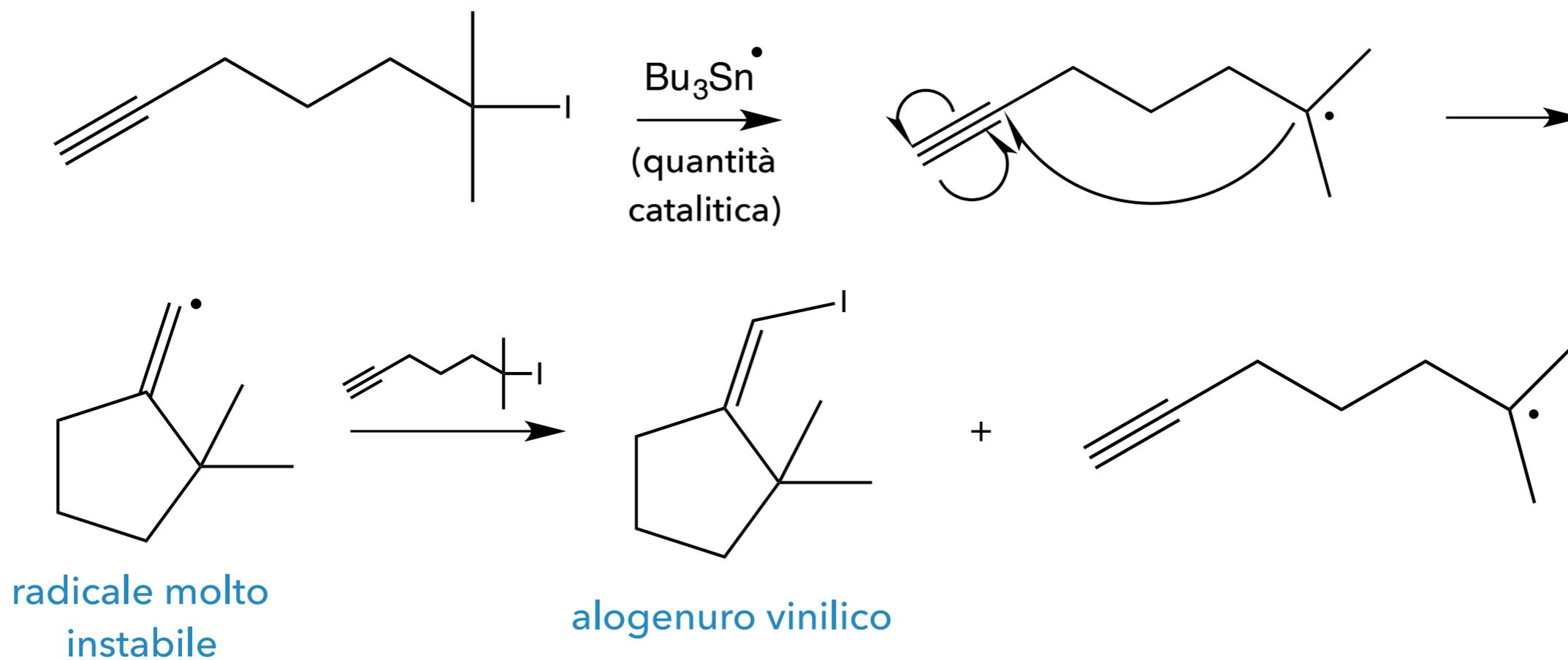
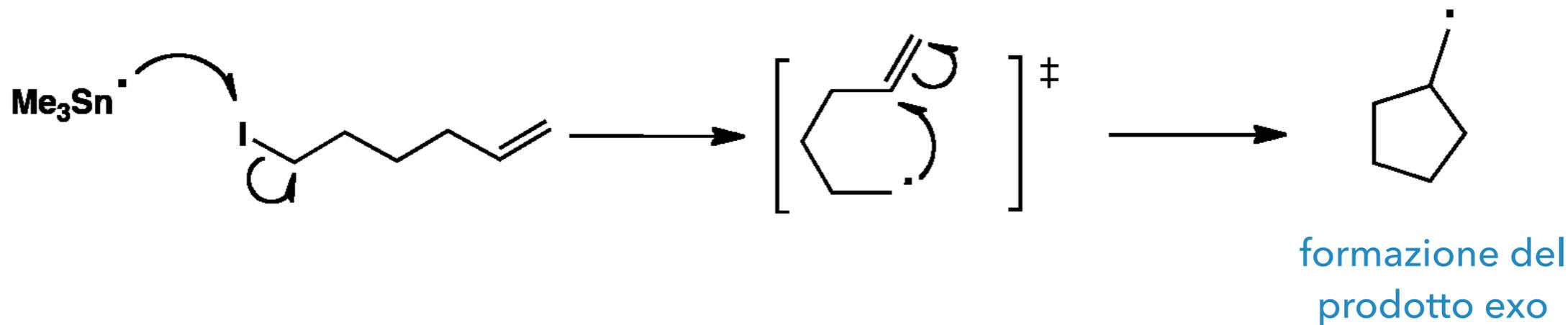
- ▶ La reazione tra alchene coniugato e Bu_3SnH genera Bu_3SnX stechiometricamente \Rightarrow workout difficile
- ▶ Aggiungendo NaBH_4 si riduce di nuovo Bu_3SnX rigenerando $\text{Bu}_3\text{SnH} \Rightarrow$ viene limitata la quantità di stannano necessaria per la reazione
- ▶ Utilizzo di mercuriale al posto di stannano: minor quantità di organometallo necessaria



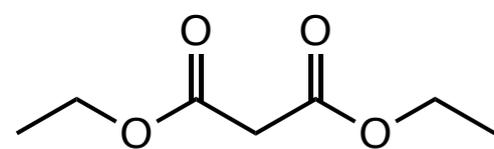
REAZIONE DI ADDIZIONE ED ELIMINAZIONE



REAZIONE DI CICLIZZAZIONE

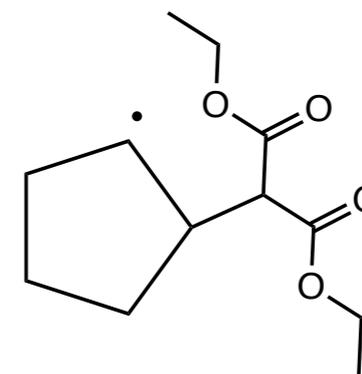
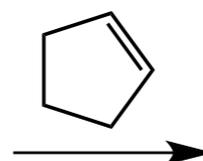
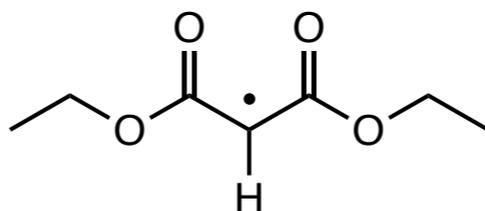


REAZIONI RADICALICHE DEI MALONATI

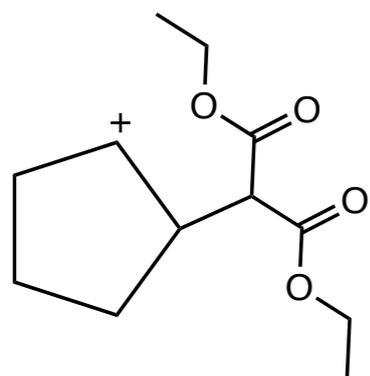


diestere

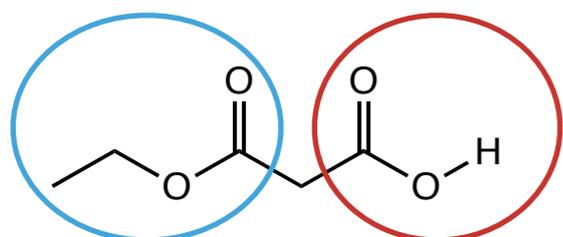
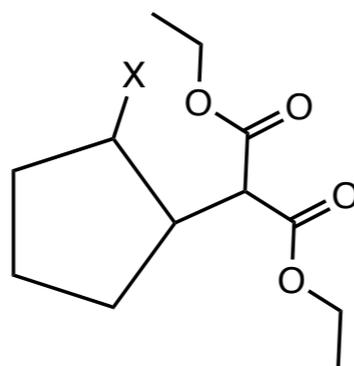
Ce(IV)



Ce(IV)

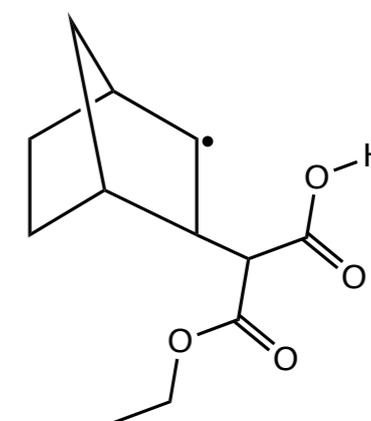
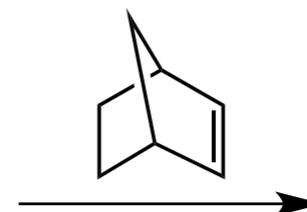
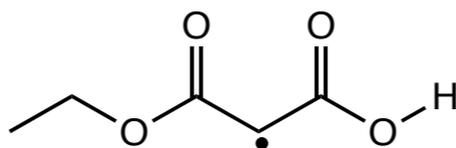


X⁻

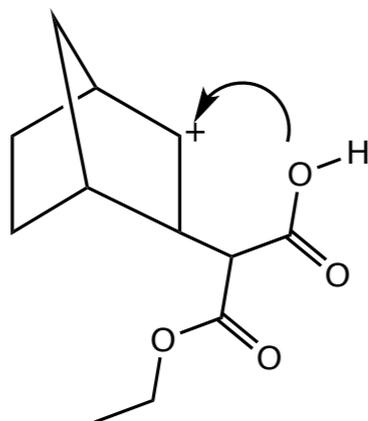


estere + carbossile

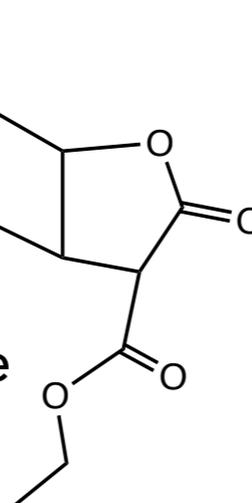
Mn³⁺



Mn³⁺



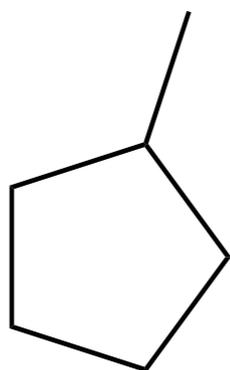
lattone



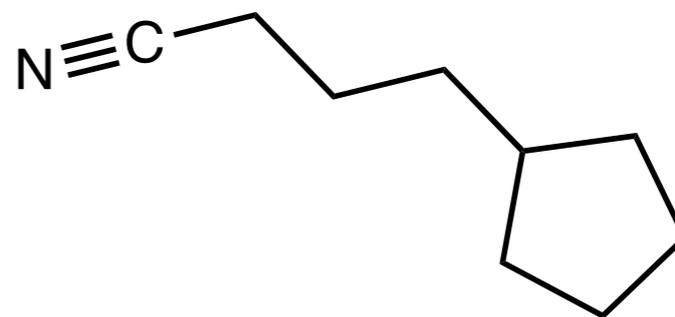
ESERCIZI RADICALI

Sintetizzare le seguenti molecole:

a)



b)



ESERCIZI RADICALI

Completare le seguenti reazioni:

