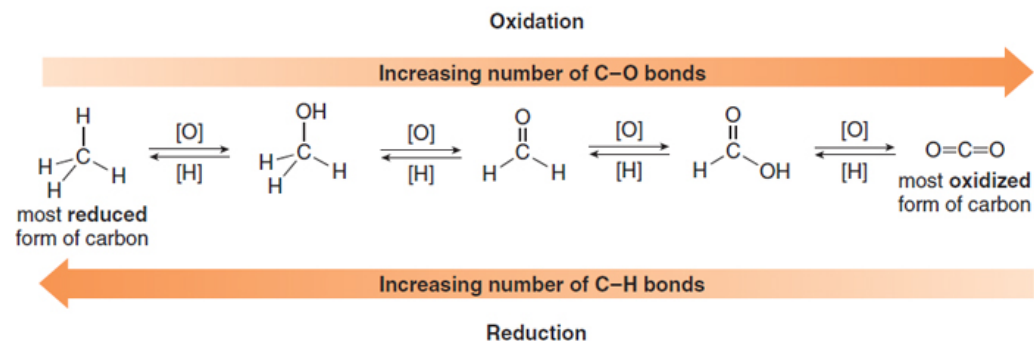
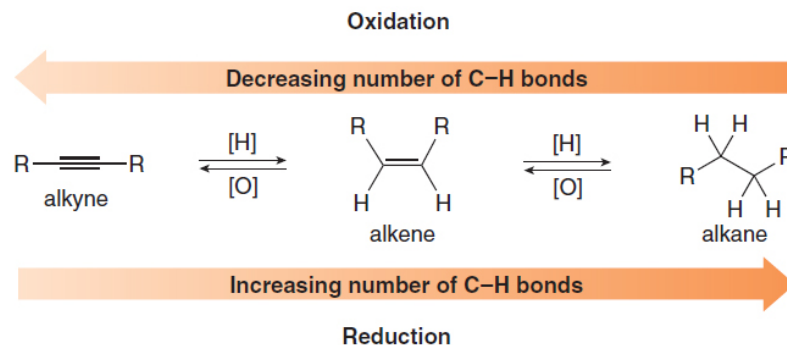


# Ossidazioni – riduzioni per i composti organici



L'ossidazione consiste nell'aumento del numero di legami C-Z (solitamente legame C-O) o un numero inferiore di legami C-H

La riduzione consiste in una decrescita del numero di legami C-Z bonds (di solito C-O) o in un incremento del numero di legami C-H

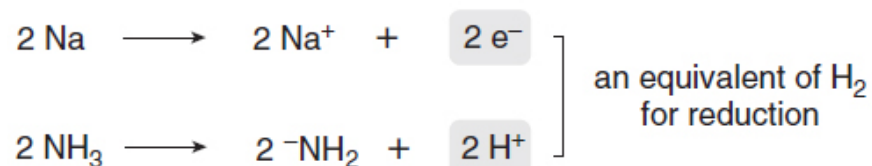


# Agenti Riducenti

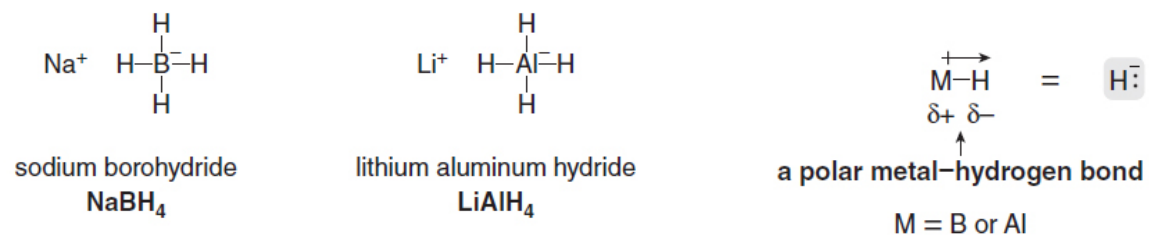
## Tre diversi metodi di riduzione

### 1. H<sub>2</sub> (solitamente in presenza di un catalizzatore)

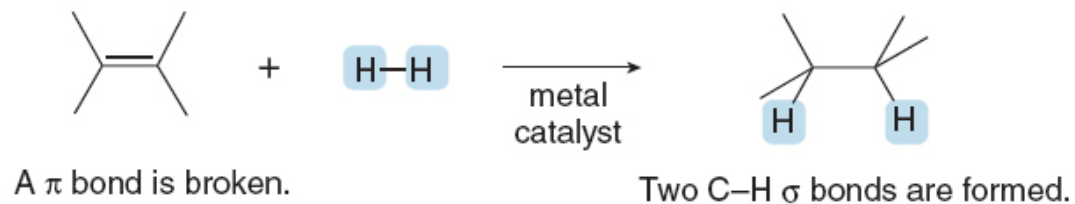
### 2° tipo: 2 H<sup>+</sup> (protoni) e 2 e<sup>-</sup> (elettroni)



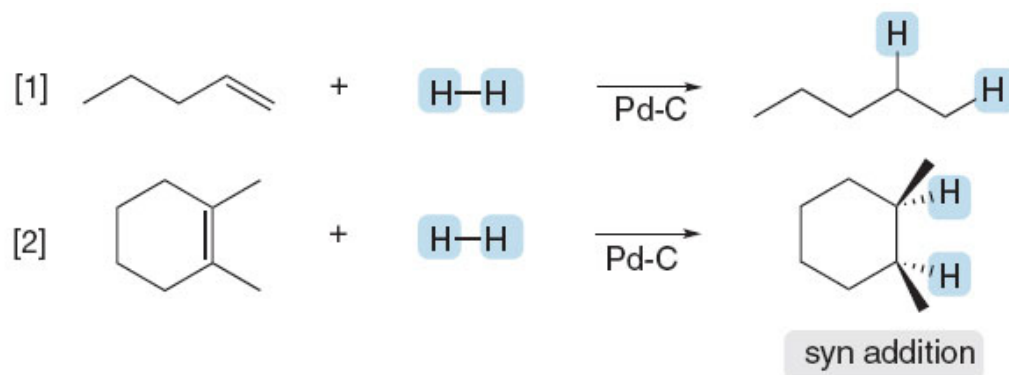
### 3° tipo: H<sup>-</sup> (idruro) e un H<sup>+</sup> (protone)



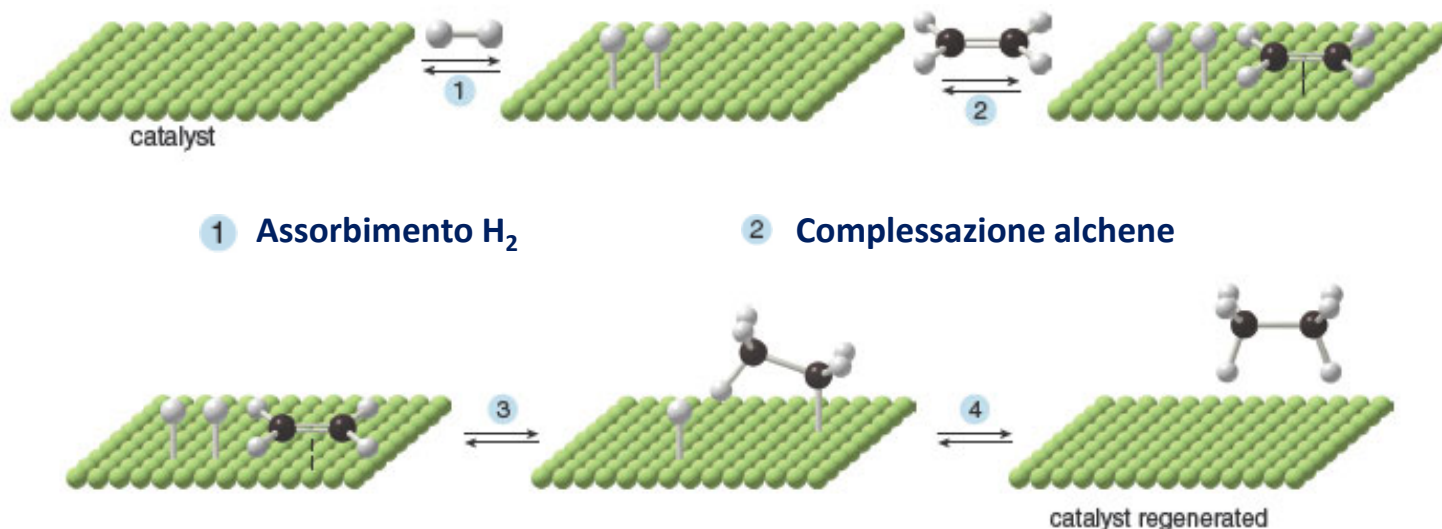
## Riduzione di alcheni (idrogenazione)



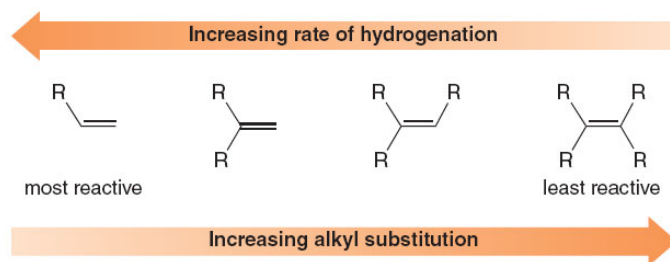
## Catalizzatori a base di Pt, Pd, Ni su supporto inerte



# Idrogenazione di alcheni metallo catalizzata (meccanismo)



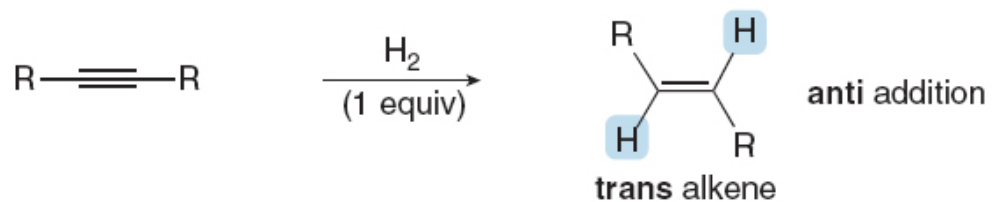
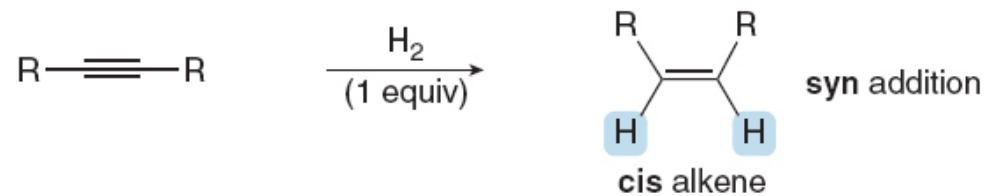
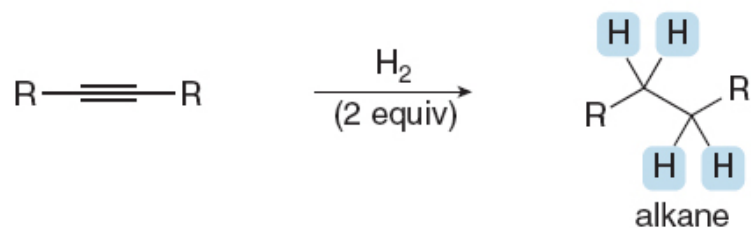
**3 - 4 H vengono trasferiti in modo sequenziale sulla stessa faccia dell'alchene**



**Reazione stereospecifica,  
sin addizione**

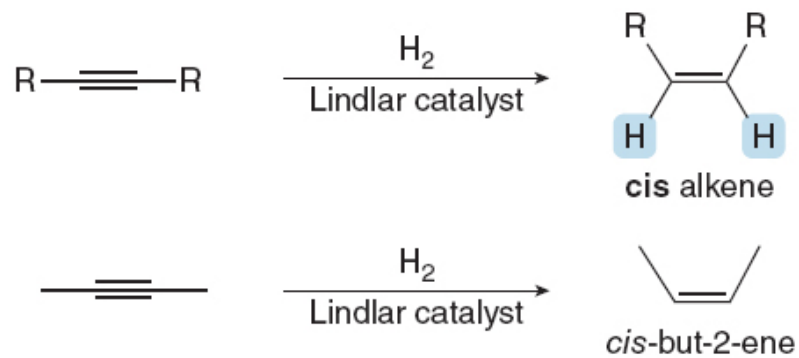
## Idrogenazione di alchini metallo catalizzata

### Sintesi di alcheni e alcani



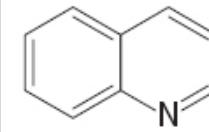
# Idrogenazione di alchini metallo catalizzata

## Sintesi di alcheni cis (Catalizzatore di Lindlar)

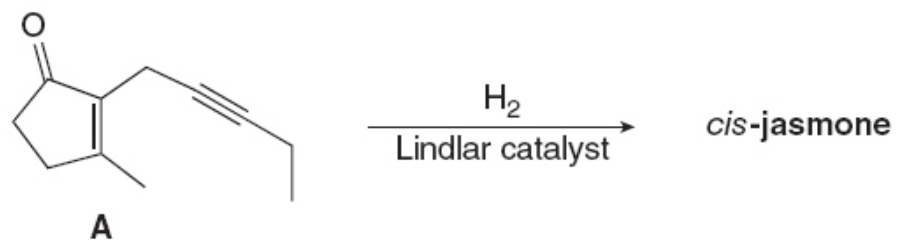


Pd on  $CaCO_3$   
+  $Pb(OCOCH_3)_2$  + quinoline

Lindlar catalyst

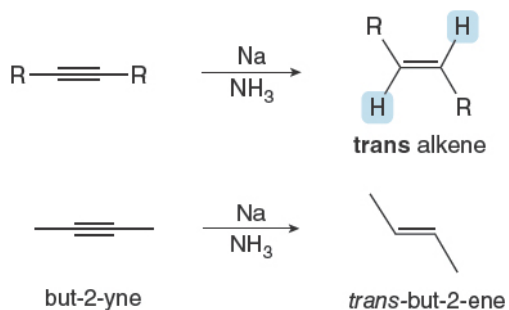


quinoline



# Idrogenazione di alchini metallo catalizzata

## Sintesi di alcheni trans (Na/NH<sub>3</sub>)



NH<sub>3</sub> (p.e.=−33 °C) Na/NH<sub>3</sub> si prepara condensando NH<sub>3</sub> a −78°C (bagno acetone/CO<sub>2</sub>(s) con un condensatore (dito freddo) a bassa temperatura (ghiaccio secco, CO<sub>2</sub> solida). Aggiungendo Na all'ammoniaca liquida si forma una soluzione blu (elettroni solvatati) che poi diventa di color bronzo metallic a maggiori concentrazioni

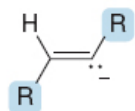
Un alchino chirale (*R*)-**A** con formula molecolare C<sub>6</sub>H<sub>10</sub> è ridotto con H<sub>2</sub>/catalizzatore di Lindlar a **B**. Quale è la struttura di **A** e **B**?

## Idrogenazione di alchini metallo catalizzata

### Sintesi di alcheni *trans* (Na/NH<sub>3</sub>) - Meccanismo

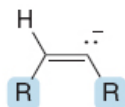


- 1 Addizione di e<sup>-</sup> al triplo legame: formazione di un radical anione.
- 2 Protonazione del radical anione (NH<sub>3</sub>): sintesi di un radicale vinilico
- 3 Addizione di un secondo elettrone: sintesi di un carbanione vinilico
- 4 Protonazione del carbanione (NH<sub>3</sub>) fornisce l'alchene *trans*



The larger R groups are farther away from each other.

This more stable vinyl carbanion forms the *trans* alkene.

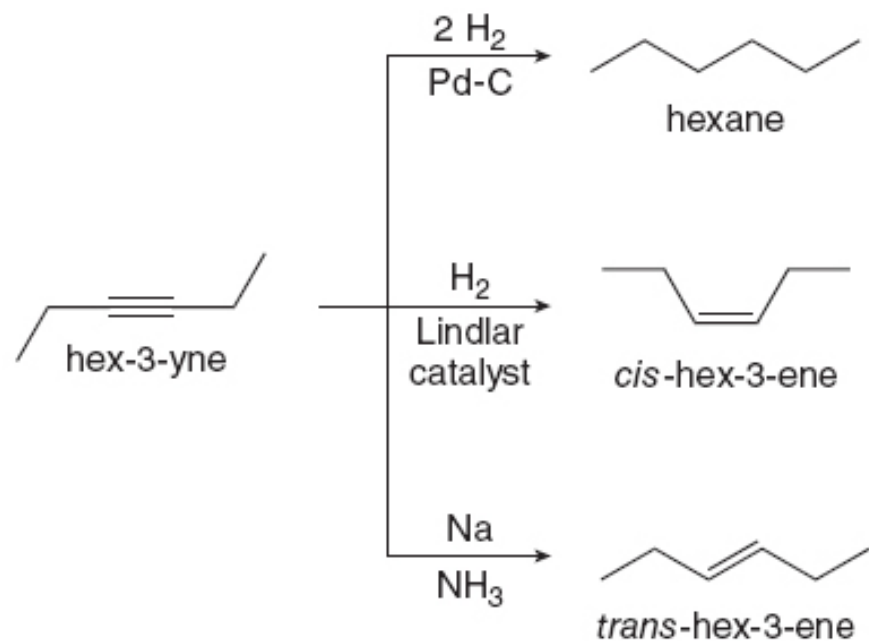


Steric interactions between closer R groups destabilize this carbanion.

**stereoselezione:  
si forma l'alchene più stabile**



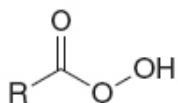
## Idrogenazione di alchini metallo catalizzata



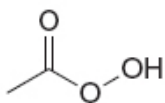
Un alchino chirale **A** ( $\text{C}_6\text{H}_{10}$ ) viene ridotto con  $\text{H}_2$  e il catalizzatore di Lindlar a **B** che contiene uno stereocentro con configurazione (R). Che struttura hanno **A** e **B**?

# Ossidazioni - Agenti Ossidanti

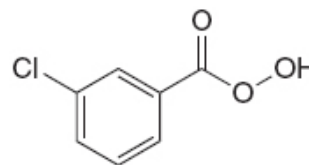
## Reagenti con legami ossigeno-ossigeno ( $O_2$ , $O_3$ , $H_2O_2$ , per-acidi)



peroxyacid

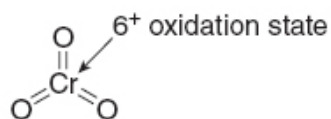


peroxyacetic acid

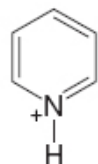


*meta*-chloroperoxybenzoic acid  
mCPBA

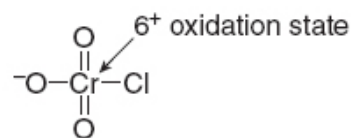
## Reagenti con legami metallo-ossigeno



chromium(VI) oxide

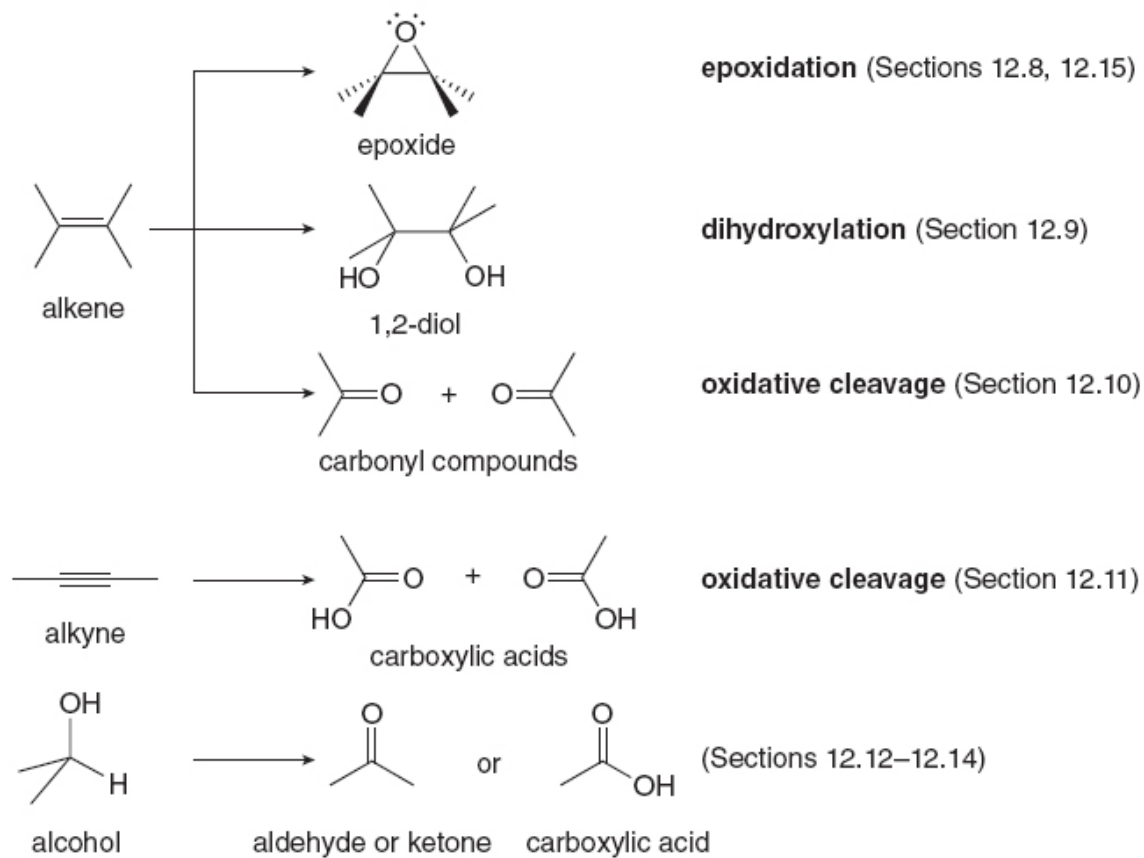


pyridinium chlorochromate

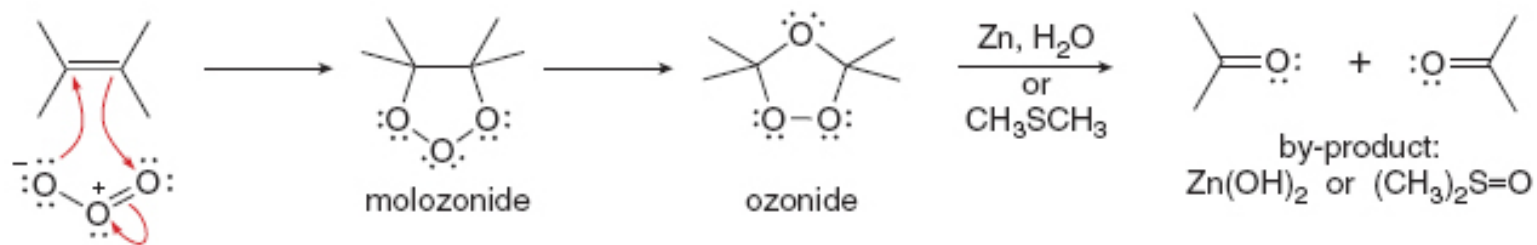


$KMnO_4$  (permanganato di potassio),  $OsO_4$  (osmio tetrossido)  $Ag_2O$  (argento(I) ossido)

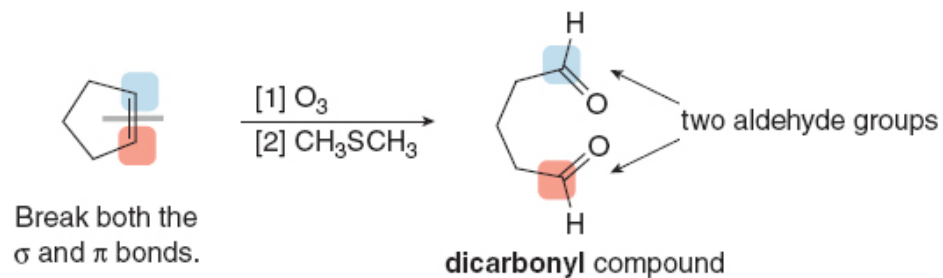
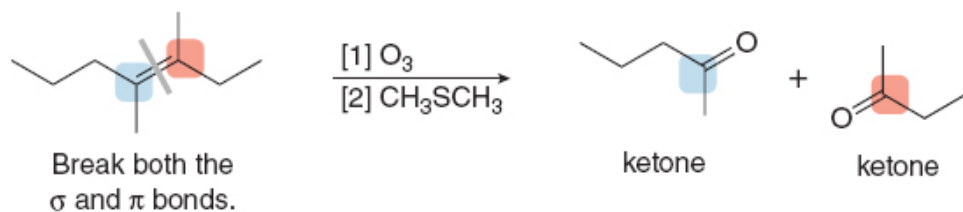
## Reazioni di ossidazione di alcheni, alchini e alcoli



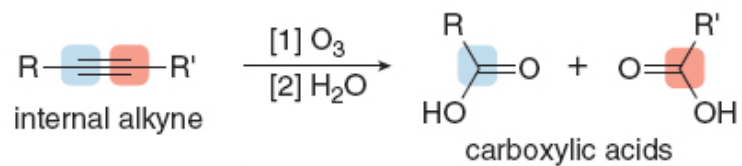
## Ozonolisi



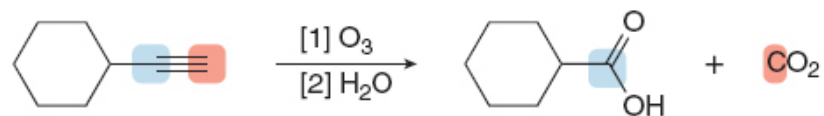
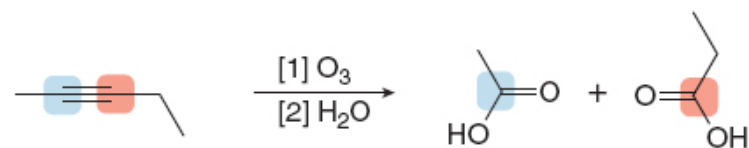
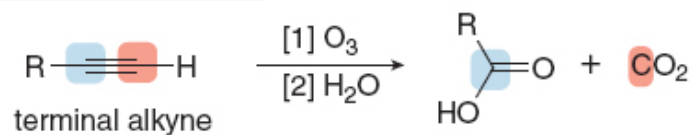
## Ozonolisi di alcheni lineari e ciclici



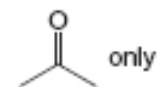
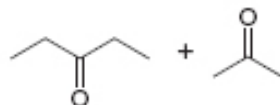
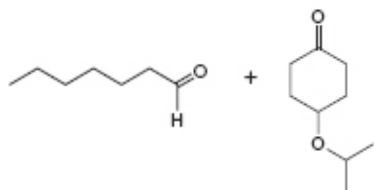
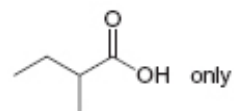
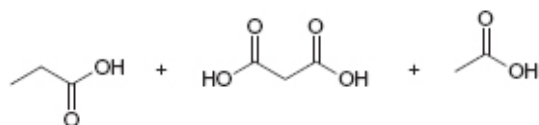
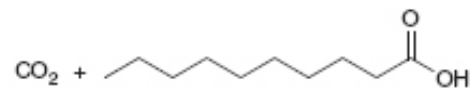
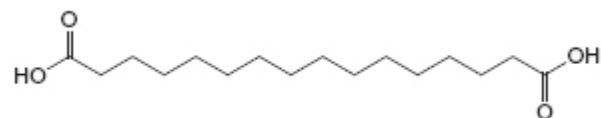
## Ozonolisi di alchini (sintesi di acidi carbossilici)



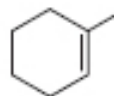
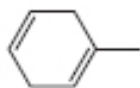
The  $\sigma$  and both  $\pi$  bonds are broken.



Da che alchene/alchino si ottengono i seguenti prodotti?



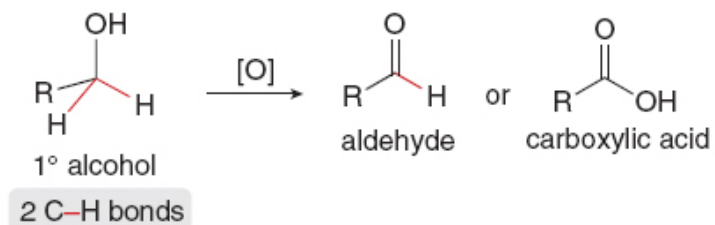
Che prodotto si ottiene per ozonolisi dei seguenti composti?



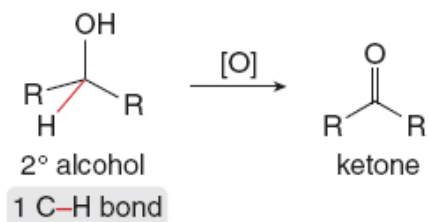
# Ossidazione di Alcoli

## Ossidazione di uno o due legami C-H

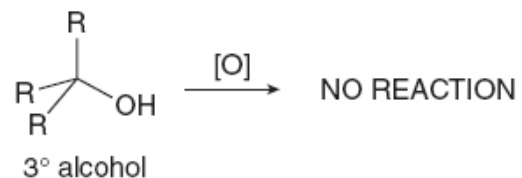
### Alcoli primari : aldeide/acido carbossilico



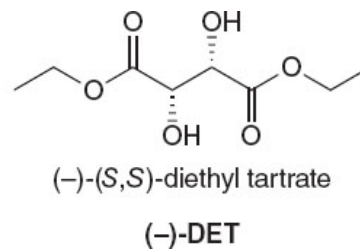
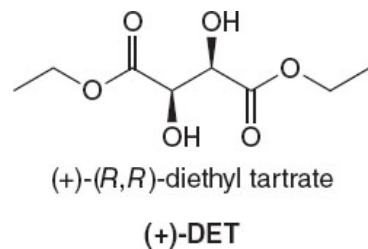
### Alcoli secondari : chetone



### Alcoli terziari : non reattivi

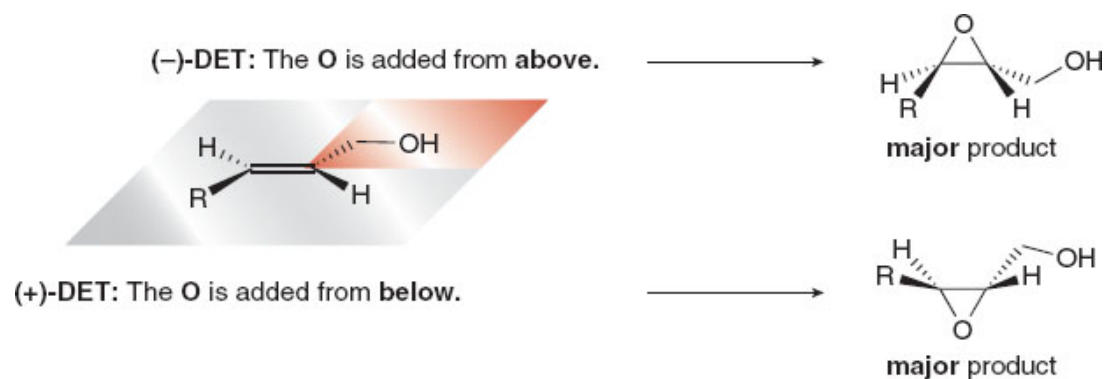


## Epossidazione di Sharpless – legante chirale



(+)-(R,R)-DET si ottiene dal (R,R)-diethyltartrato sottoprodotto dell'industria vinicola

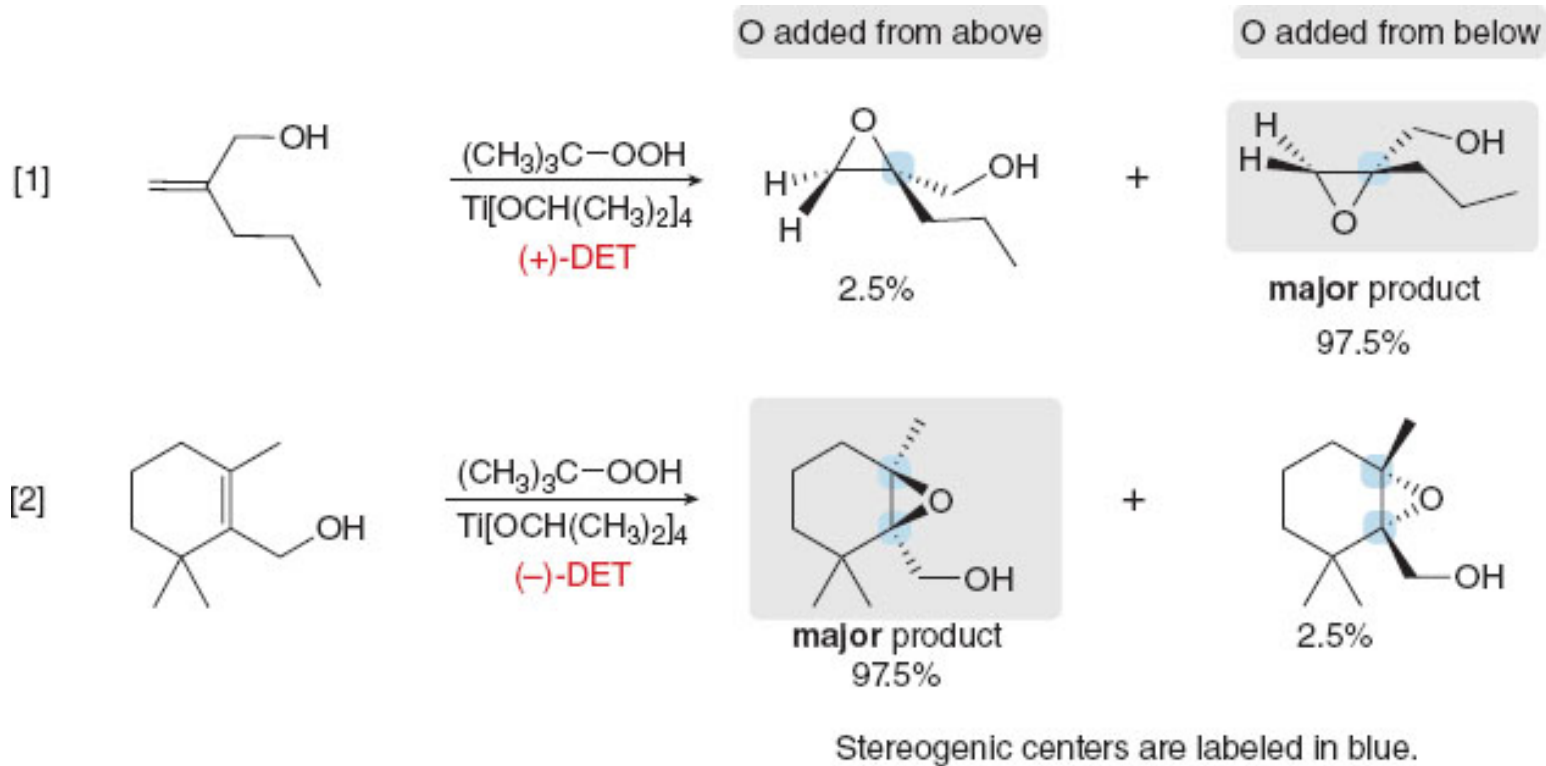
### Modello Mnemonico



**Il catalizzatore consente l'ossidazione solamente degli alcoli allilici**

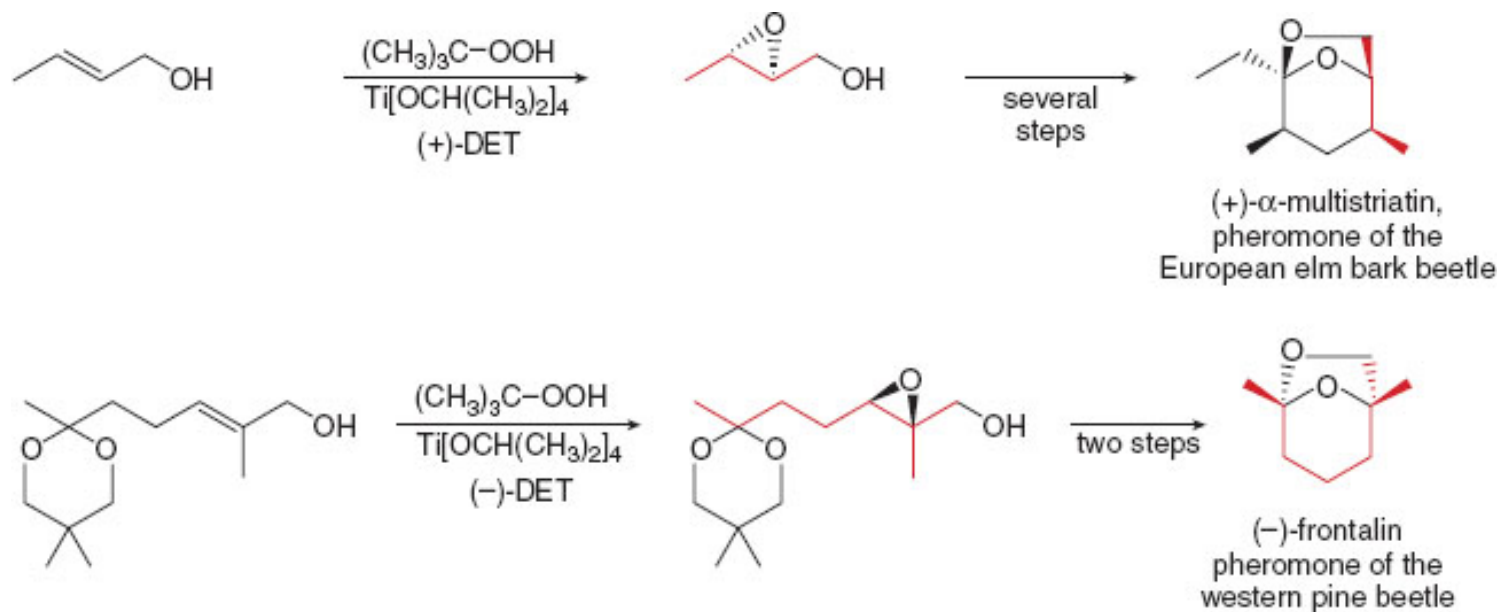


## Eossidazione di Sharpless



## Eossidazione di Sharpless

### Sintesi stereoselettiva di feromoni - (+)- $\alpha$ -multistriatin e (-) frontalin

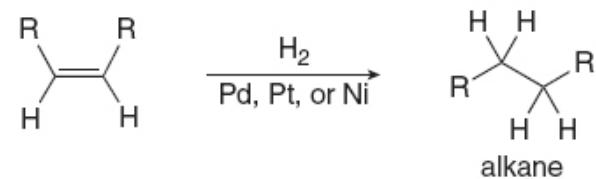


- The bonds in the products that originate from the epoxide intermediate are indicated in red.

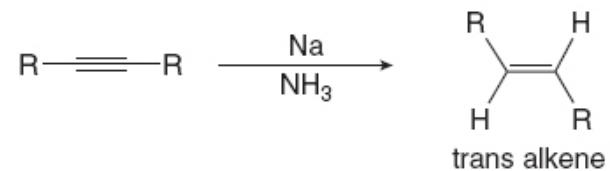
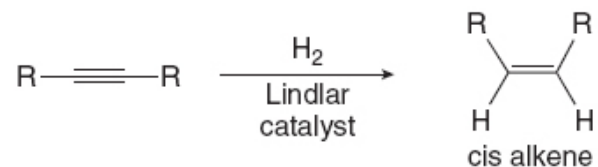
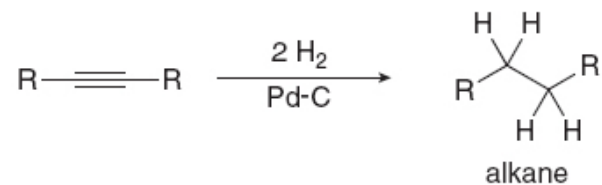
## Ossidazioni e Riduzioni

Esercizi

### Reduction of alkenes—Catalytic hydrogenation

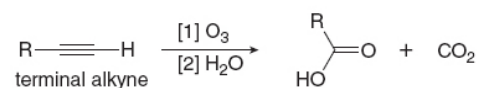
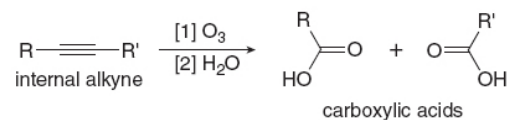
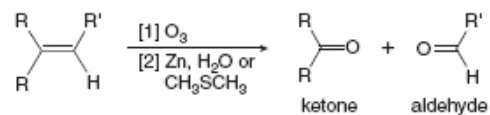


### Reduction of alkynes

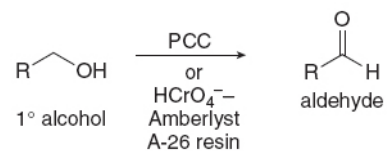


## Ossidazioni e Riduzioni

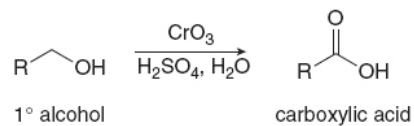
### Oxidative Cleavage



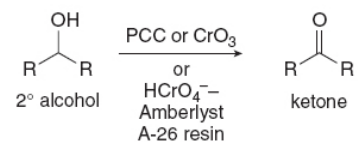
### Ossidazione di Alcoli



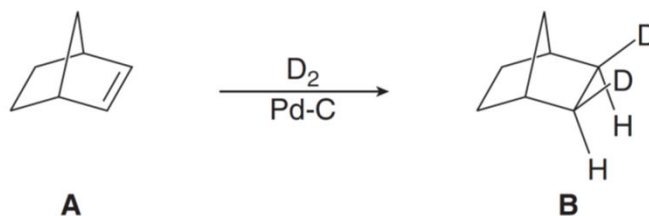
### Swern (DMSO/CIC(O)C(O)Cl)



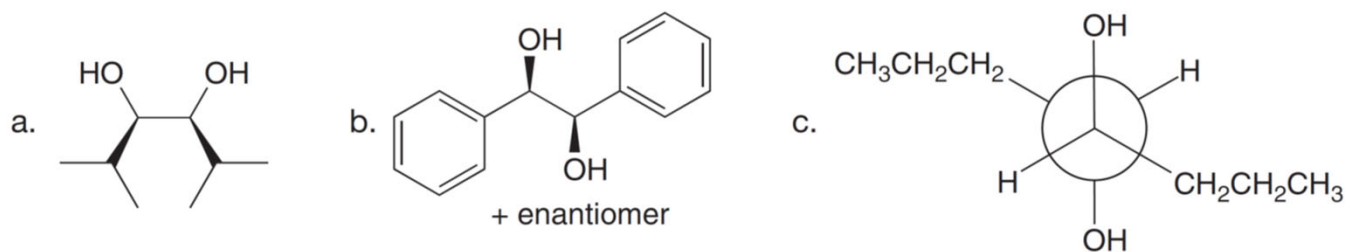
### IBX/DMP



- 12.43** Hydrogenation of alkene **A** with  $D_2$  in the presence of Pd-C affords a single product **B**. Keeping this result in mind, what compound is formed when **A** is treated with each reagent: (a) mCPBA; (b)  $Br_2$ ,  $H_2O$  followed by base? Explain these results.

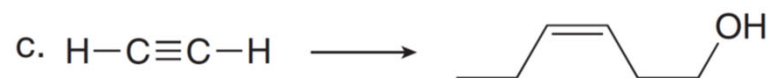
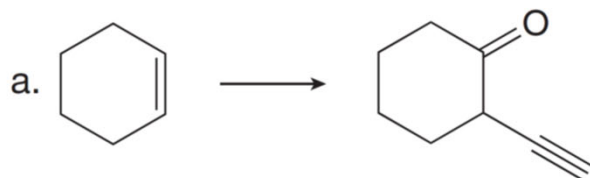


- 12.44** What alkene is needed to synthesize each 1,2-diol using [1]  $OsO_4$  followed by  $NaHSO_3$  in  $H_2O$ ; or [2]  $CH_3CO_3H$  followed by  $^-OH$  in  $H_2O$ ?

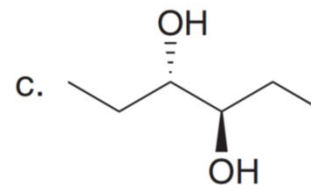
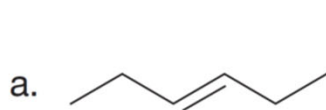


**12.56** One compound that contributes to the “seashore smell” at beaches in Hawai‘i is dictyopterene D', a component of a brown edible seaweed called limu lipoa. Hydrogenation of dictyopterene D' with excess  $H_2$  in the presence of a Pd catalyst forms butylcycloheptane. Ozonolysis with  $O_3$  followed by  $(CH_3)_2S$  forms  $CH_2(CHO)_2$ ,  $HCOCH_2CH(CHO)_2$ , and  $CH_3CH_2CHO$ . What are possible structures of dictyopterene D'?

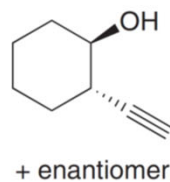
**12.66** Devise a synthesis of each compound from the indicated starting material, organic compounds containing one or two carbons, and any other required reagents.



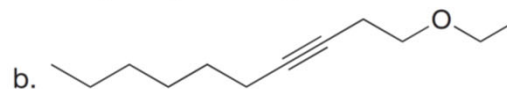
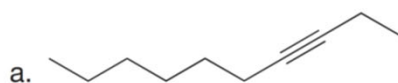
**12.69** Devise a synthesis of each compound from  $CH_3CH_2OH$  as the only organic starting material; that is, every carbon in the product must come from a molecule of ethanol. You may use any other needed inorganic reagents.



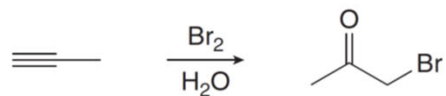
11.53 Devise a synthesis of the following compound from cyclohexene and acetylene. You may use any other inorganic reagents.



11.54 Devise a synthesis of each compound. You may use  $\text{HC}\equiv\text{CH}$ , ethylene oxide, and alkyl halides as organic starting materials and any inorganic reagents.



11.61 Draw a stepwise mechanism for the following reaction.



**11.52** Devise a synthesis of each compound using  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$  as the starting material. You may use any other organic compounds or inorganic reagents.

