

# 1,3 dipole cycloaddition; [3,2] cycloadditions

=> important for Med. Chem

C434

(also DA)

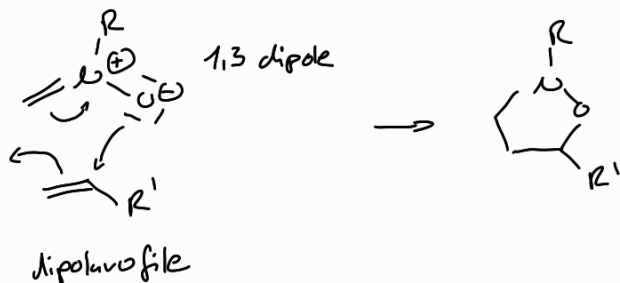
1,3 dipole has  $\equiv$  and  $-$  => 4e<sup>-</sup> on 3 atoms

ex

Nitron

LUMO

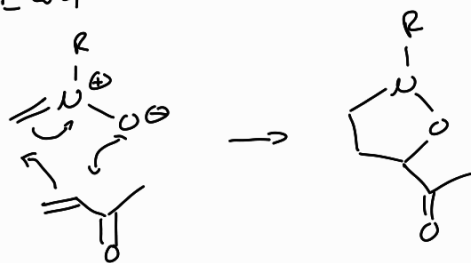
HOMO



With EWG

HOMO

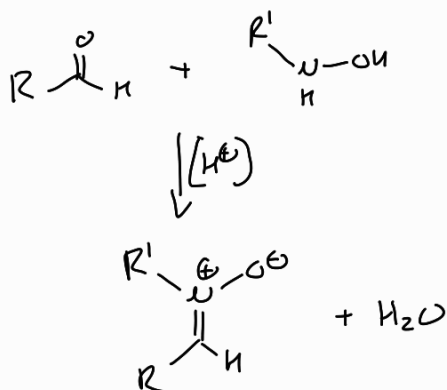
LUMO



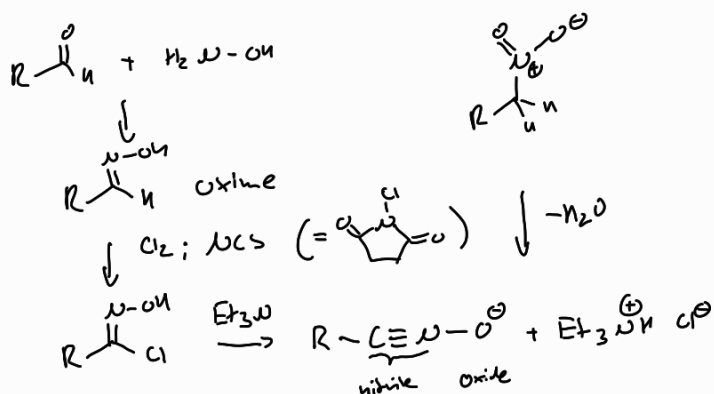
=  
DA

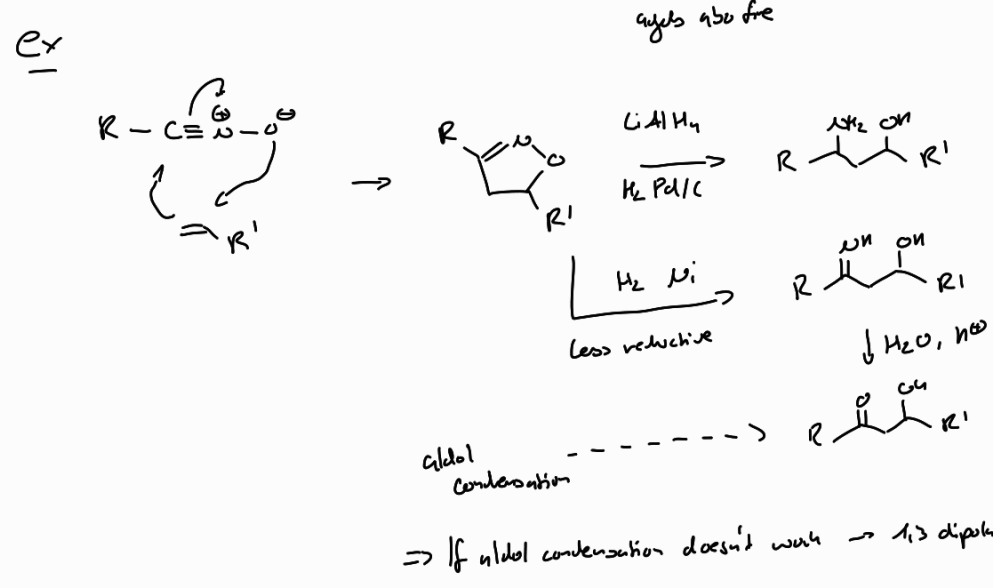
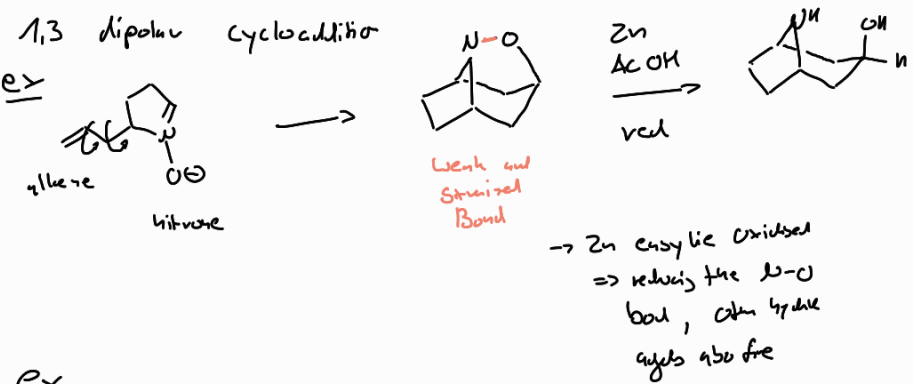
=> for [3,2] cycloaddition the reaction between dipole and dipolarophile is not always the same FMO as in DA  
-> decide depends on functional groups

Make Nitrons

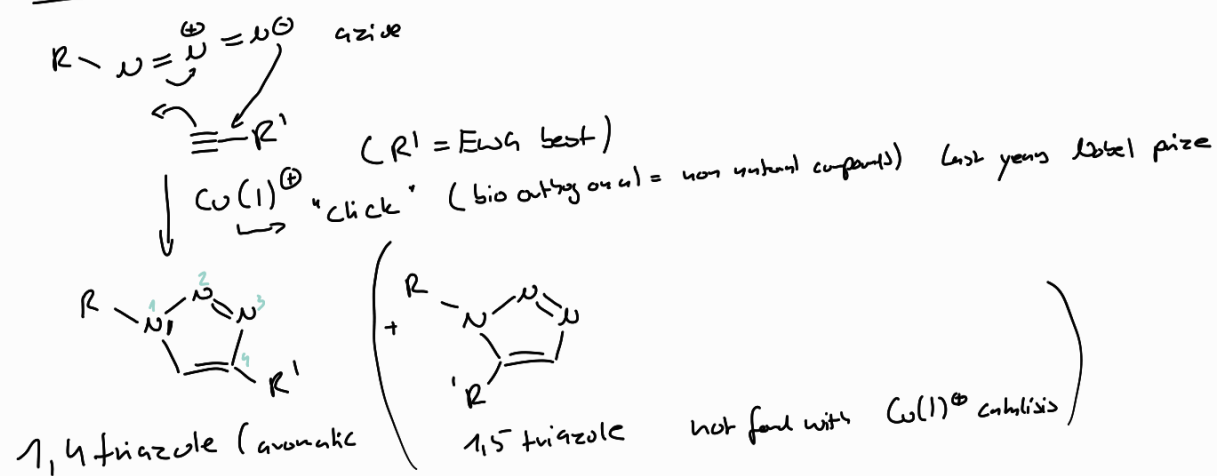


Nitrile oxides

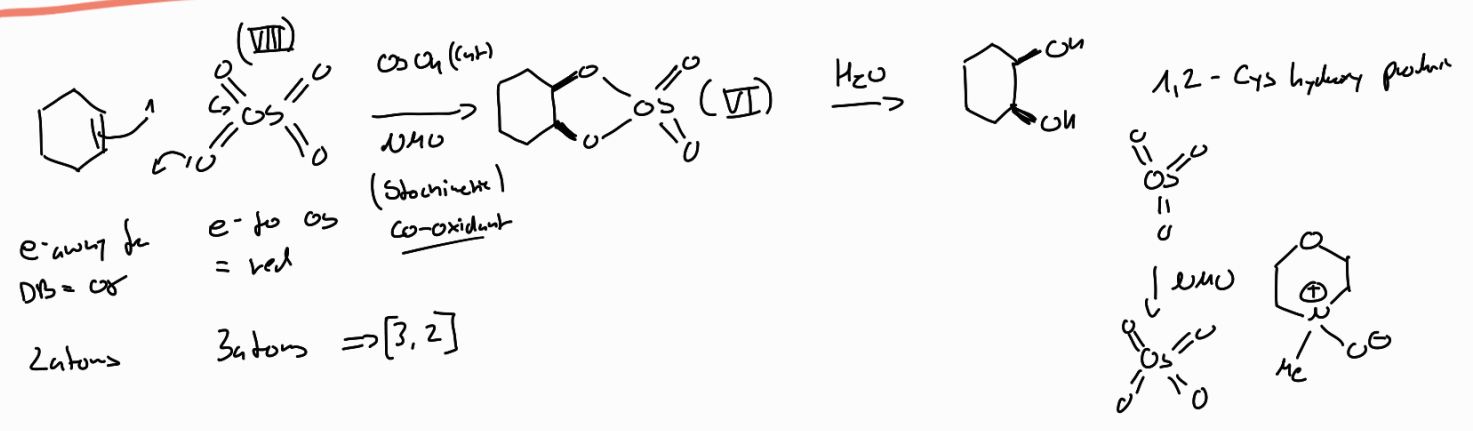




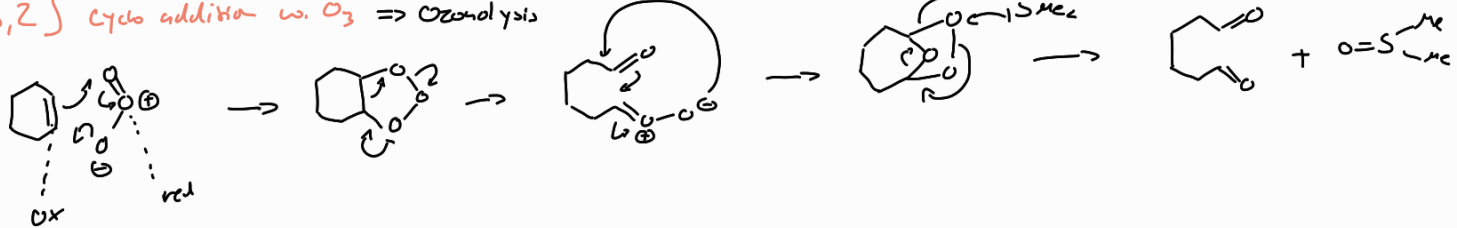
Other 1,3 dipolar cycloadditions



[3,2] cycloadditions with  $\text{OsO}_4$



[3,2] cyclo addition w.  $O_3 \Rightarrow$  ozonolysis

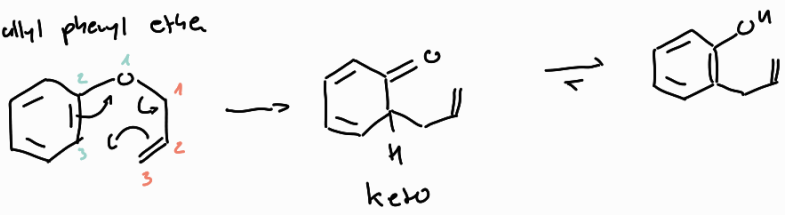


Signatropic rearrangement  
(+ electrocyclic reactions)

Ch 35

Claisen rearrangement = [3,3] signatropic rearrangement

allyl phenyl ether



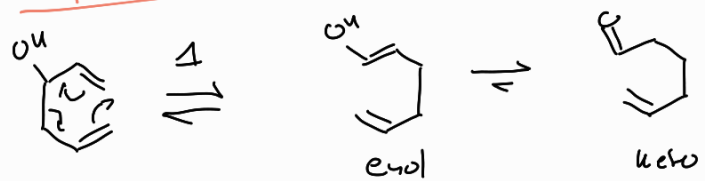
Aliphatic version - Claisen Cope  
(not aromatic)



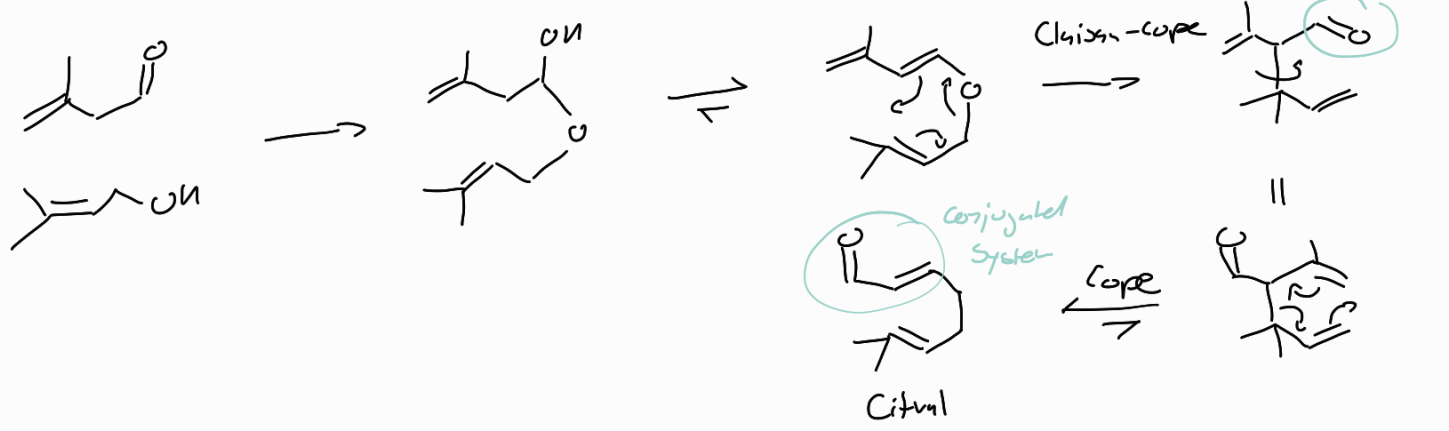
$\gamma$ - $\delta$  unsaturated carbonyls

Diels Alder  $\Rightarrow$  2  $C=C$  vs. 1  $C=C$ , 1  $C=O$   
(Steyer bond)

Cope rearrangement

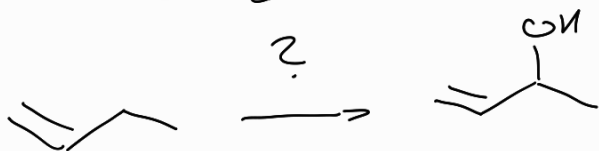


ex Citral synthesis (test w/ type)

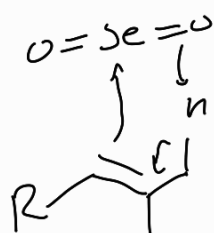


# [2,3] sigmatropic rearrangement

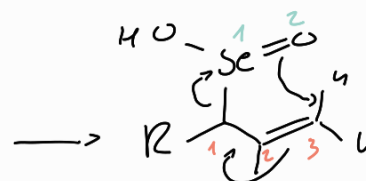
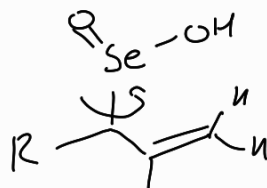
SeO<sub>2</sub> mediated allylic oxidation



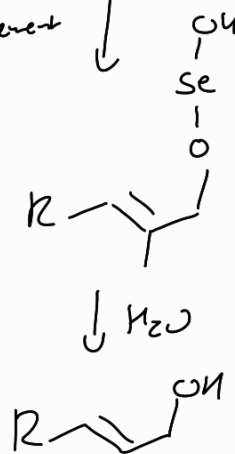
ex



$[4+2]$   
cyclo addition



[2,3]  
rearrangement



Se(OH)<sub>2</sub>