

Cycloadditions To Alkenes And Alkynes

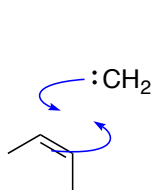
from chapter(s) _____ in the recommended text

A. Introduction

.

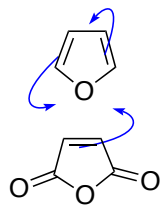
B. Nomenclature Of Cycloadditions

[3 + 2] could



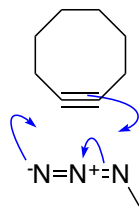
[2+1]

cyclopropanation



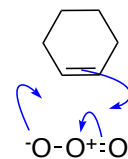
[4+2]

Diels-Alder



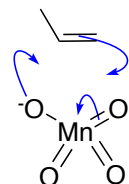
[2+3]

click reaction



[2+3]

ozonolysis



[2+3]

dihydroxylation

C. Carbene Additions [2 + 1] (Cyclopropanations)

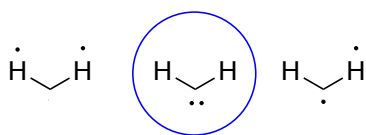
two: true.

6 electrons in the valence shell of carbon.

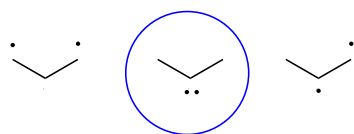
4.

is not

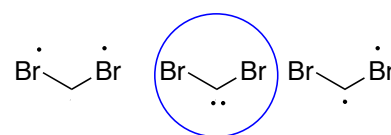
an empty p-orbital, ie singlet
a diradical structure, ie triplet



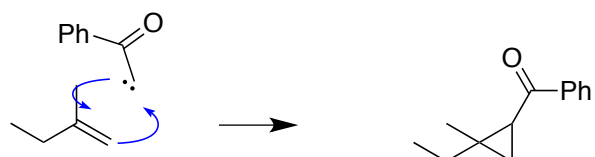
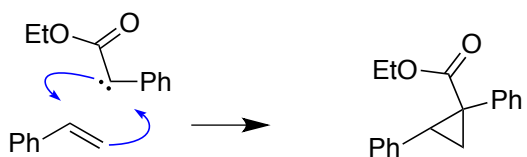
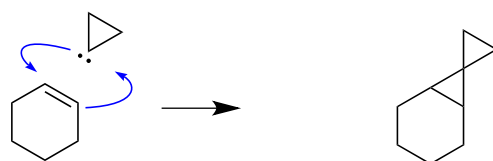
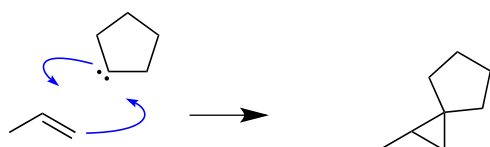
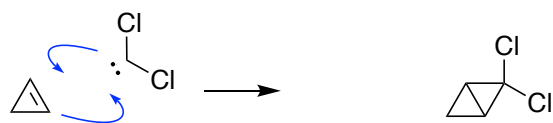
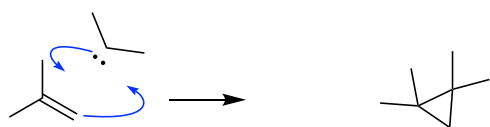
carbene



dimethylcarbene



dibromocarbene



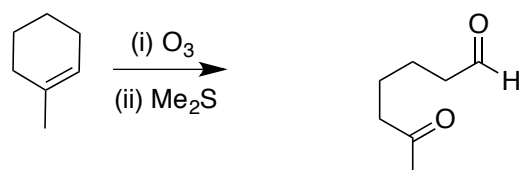
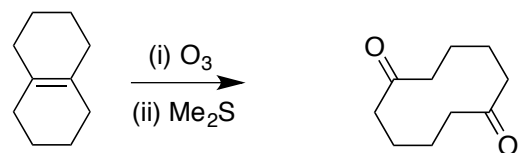
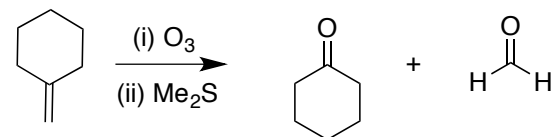
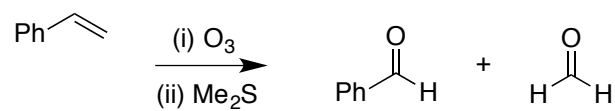
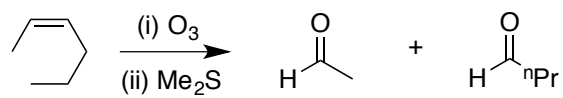
show only trans-product

show only trans-product

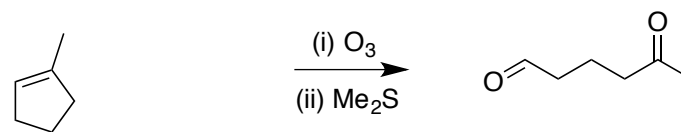
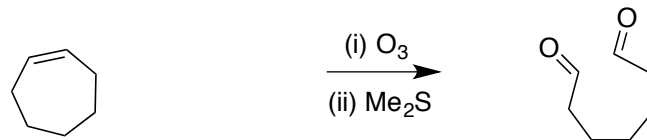
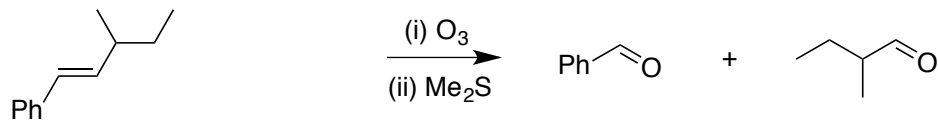
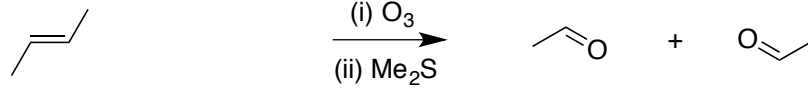
spiro-compounds.

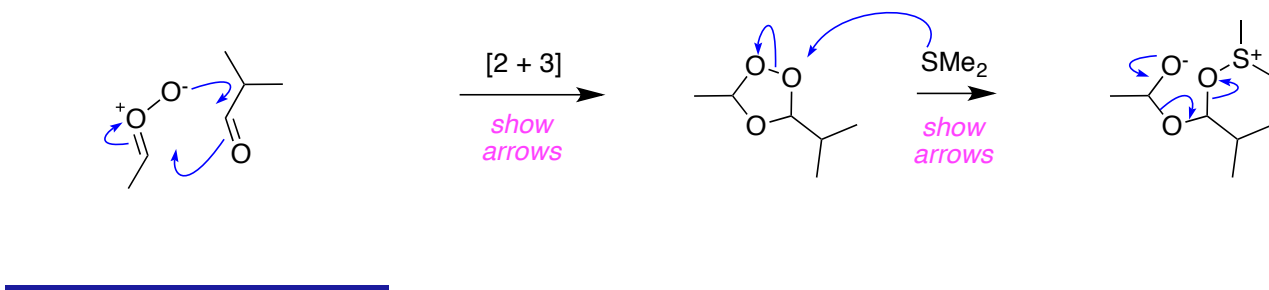
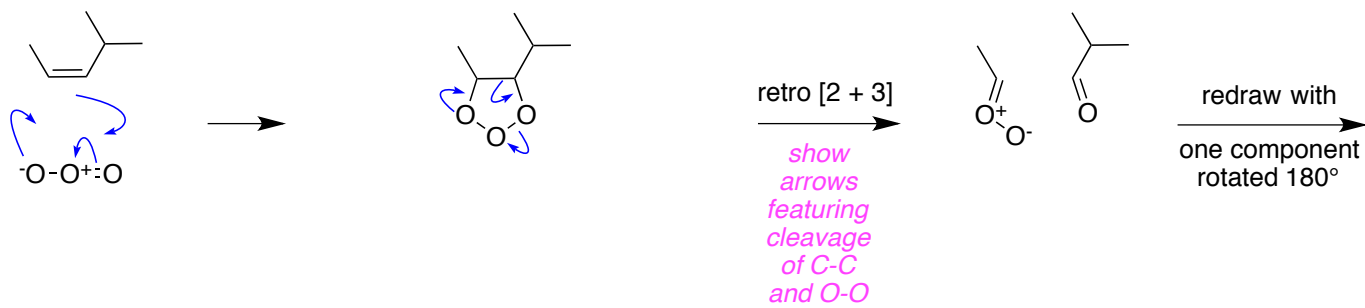
D. Ozonolysis [2 + 3]

a sea breeze / don't smell it you clown, it's highly toxic (
ozonolysis,
aldehydes / ketones

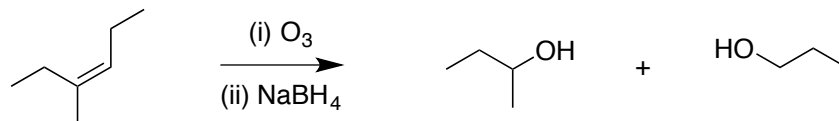


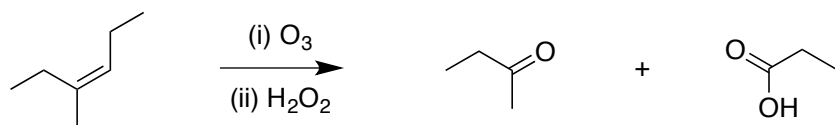
ring cleavage to 2 and 3 atoms components.





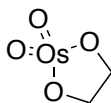
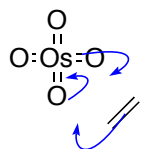
reduced
oxidized



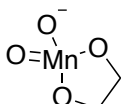
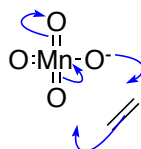


E. Dihydroxylation [2 + 3]

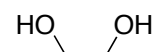
A dihydroxylation adds 2



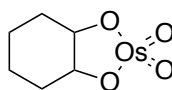
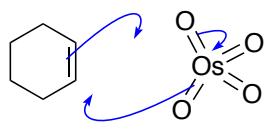
hydrolysis
→
then remove
metal salts



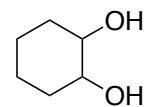
hydrolysis
→
then remove
metal salts



syn face specificity.



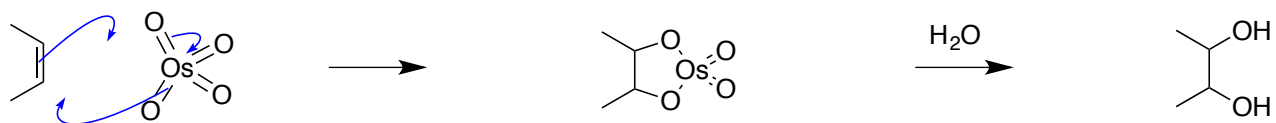
H₂O
→



osmate ester

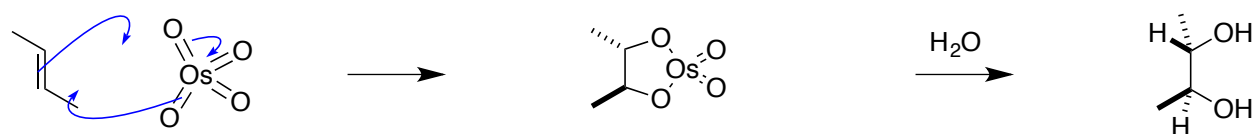
diol





osmate ester

diol

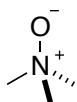


osmate ester

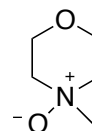
diol

cis.

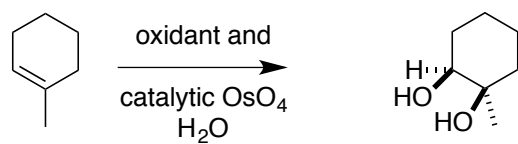
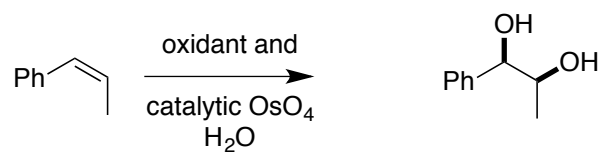
This is *unlike*
trans addition of



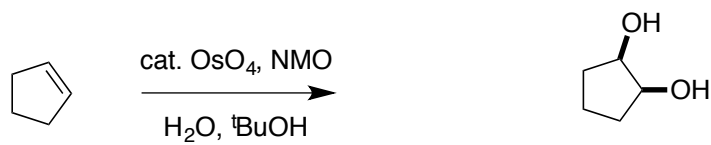
trimethylamine-N-oxide

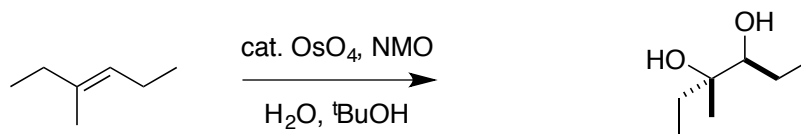


NMO



show stereochemistry

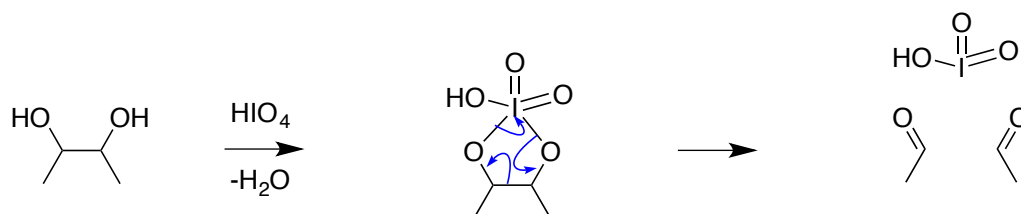


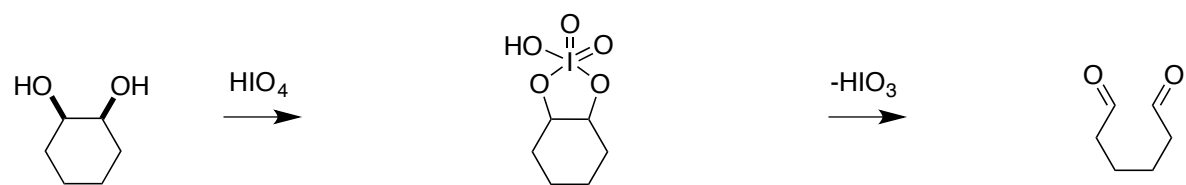


F. Periodate Cleavage

+7 oxidation state; it is *reduced*

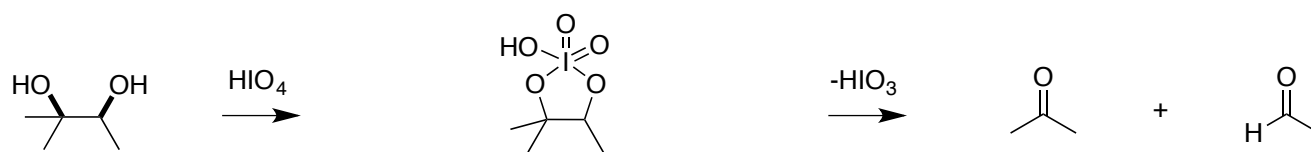
+5





periodate intermediate

products



periodate intermediate

products

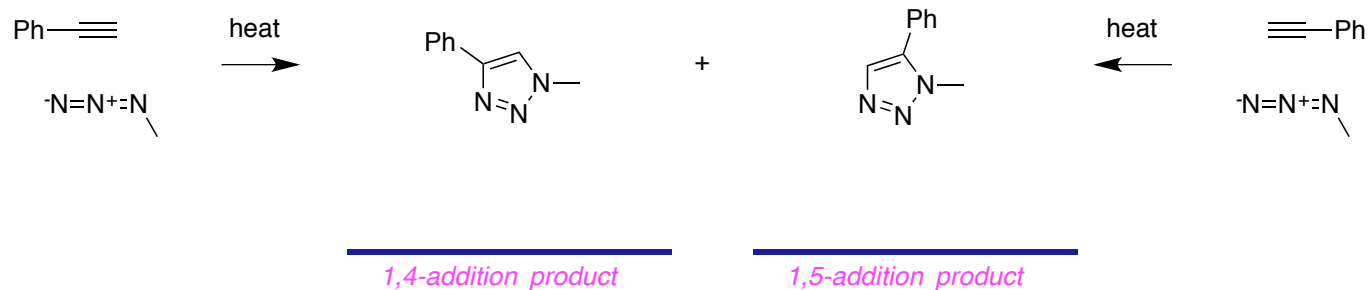
G. Azide-Alkyne “Click Reactions” [2 + 3]

at the end of a chain.

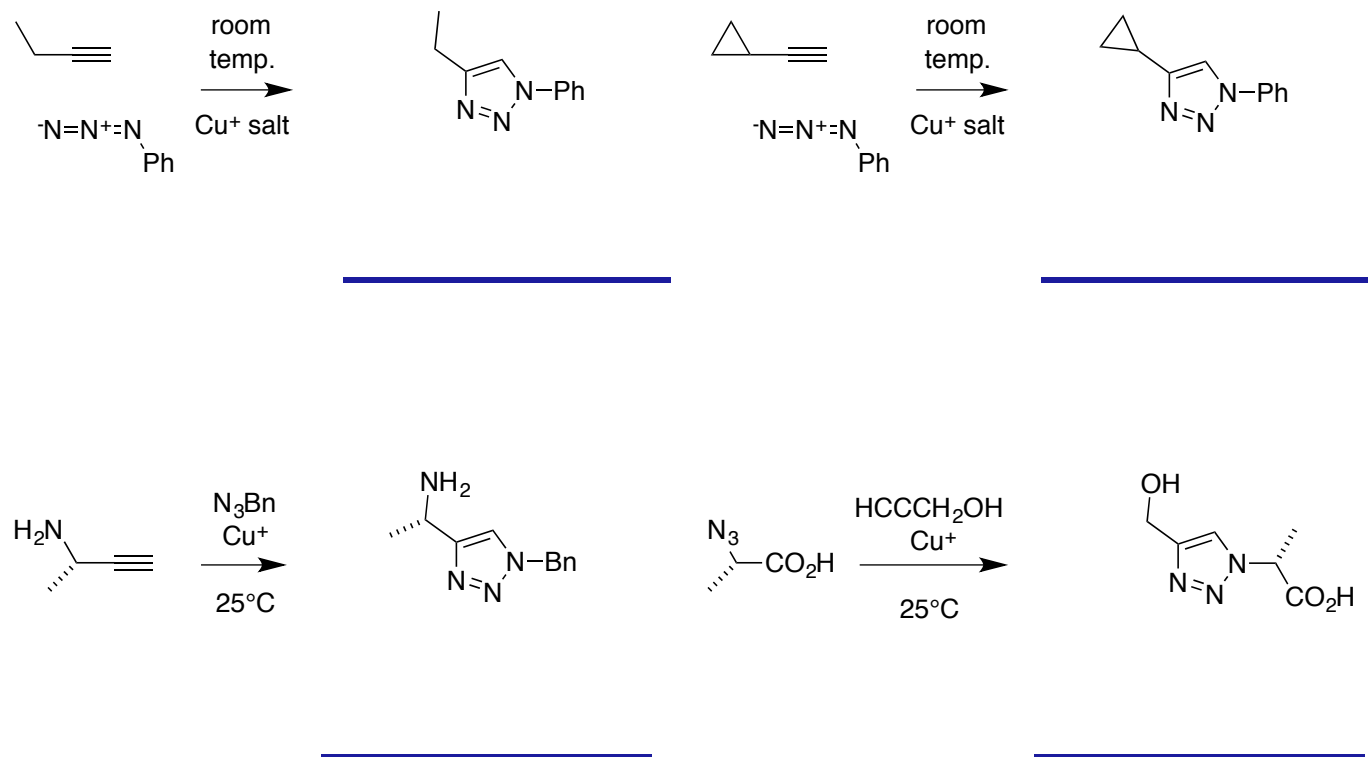
[3 + 2]

regioisomers

regioselective.



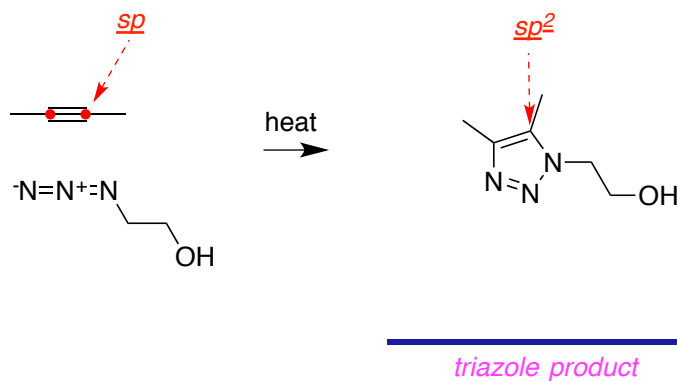
chemoselective.



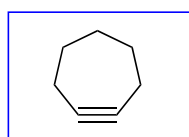
none

chemoselective.

less stable



180
120°.



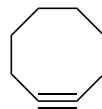
cycloheptyne

3



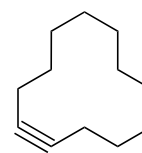
cyclopropyne

4



cyclooctyne

2



cycloundecyne

1

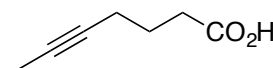
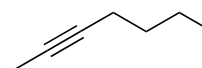
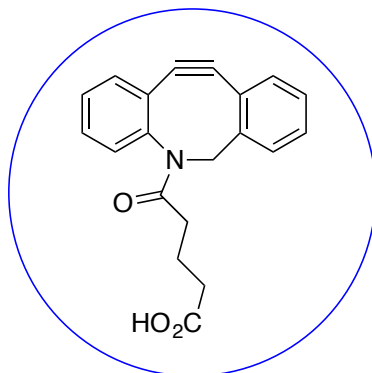
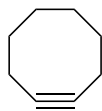
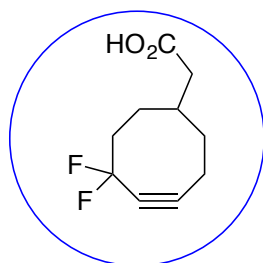
hydrogenation

most strained, ie *cyclopropyne*

sp³, thereby making those carbon atoms

sp³ (or sp² for partial hydrogenation) thereby making those carbon atoms more

sp², thereby making those carbon atoms more



can
do not need