Cycloadditions To Alkenes And Alkynes

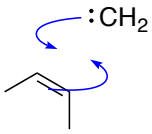
from chapter(s) _____ in the recommended text

A. Introduction

.

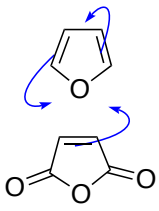
B. Nomenclature Of Cycloadditions

[3 + 2] could



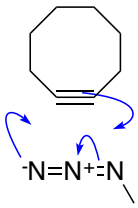
[2+1]

cyclopropanation



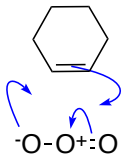
[4+2]

Diels-Alder



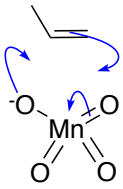
[2+3]

click reaction



[2+3]

ozonolysis



[2+3]

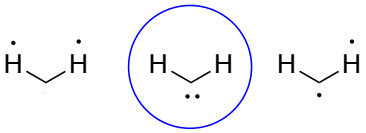
dihydroxylation

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

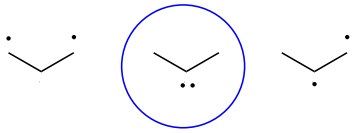
two: *true*.

6 electrons in the valence shell of carbon.
4.
is not

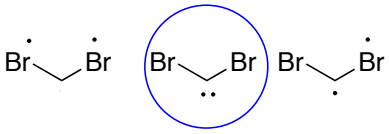
an empty p-orbital, *ie* *singlet*
a diradical structure, *ie* *triplet*



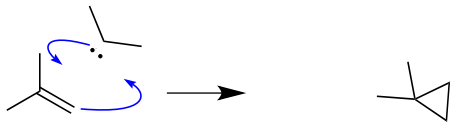
carbene

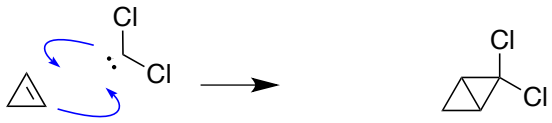


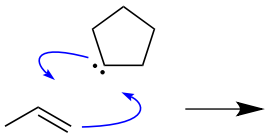
dimethylcarbene

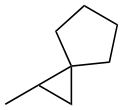


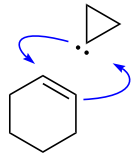
dibromocarbene

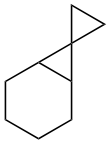


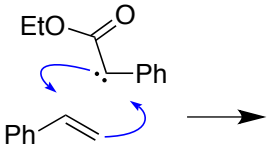


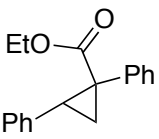




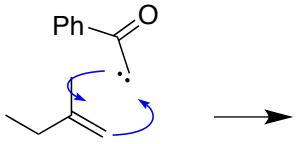


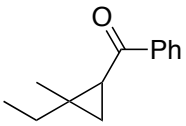






show only trans-product



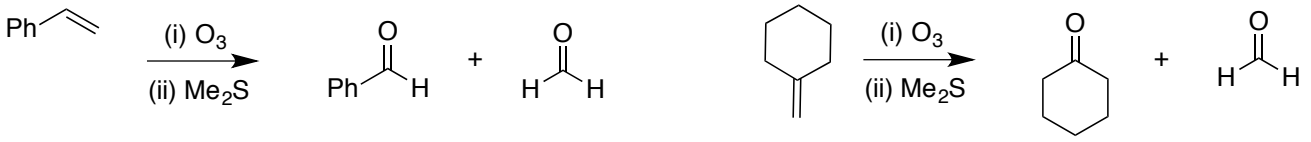


show only trans-product

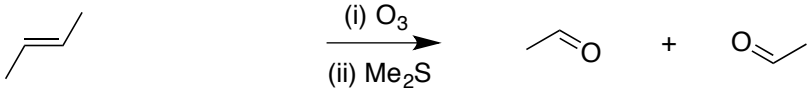
*spiro-*compounds.

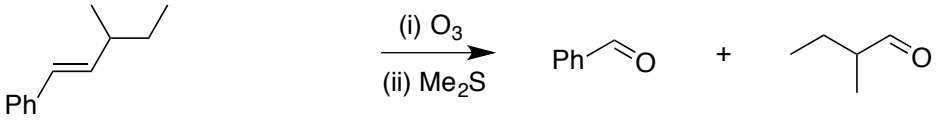
D. Ozonolysis [2 + 3]

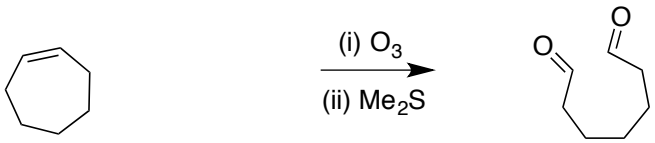
a sea breeze / don't smell it you clown, it's highly toxic (
ozonolysis,
aldehydes / ketones

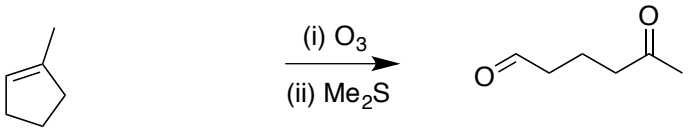


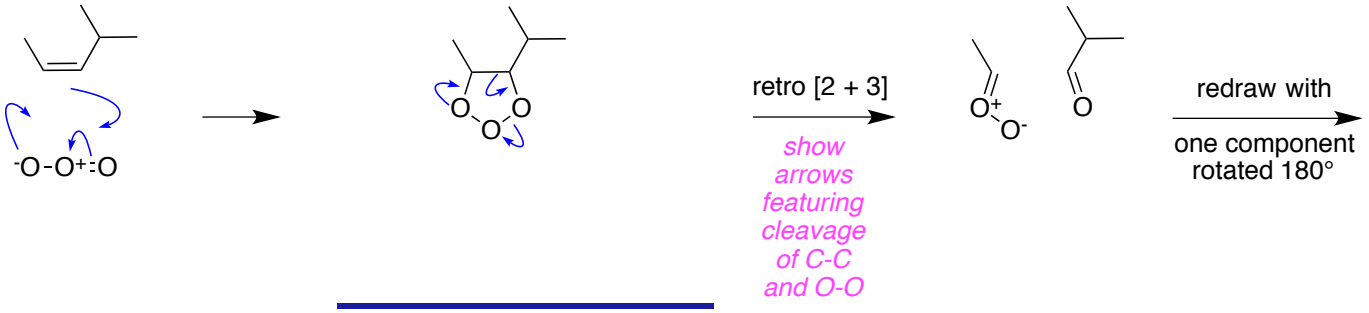
ring cleavage to 2 and 3 atoms components.

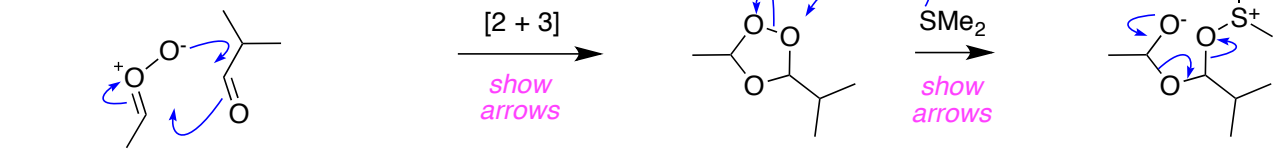

(i) O3
(ii) Me2S
O
+
O


Ph
(i) O3
(ii) Me2S
Ph
O
+
O

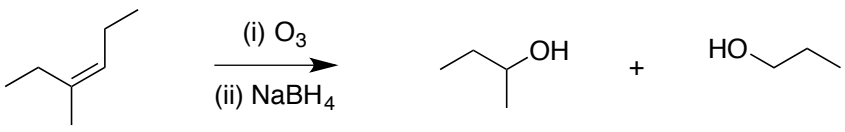

(i) O3
(ii) Me2S
O
O


(i) O3
(ii) Me2S
O
O


retro [2 + 3]
show arrows featuring cleavage of C-C and O-O
redraw with
one component rotated 180°

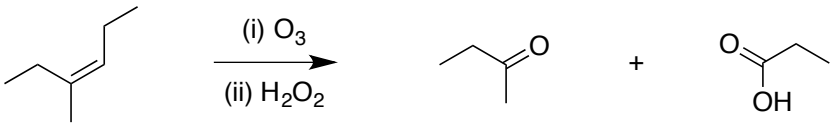

[2 + 3]
show arrows
SMe2
show arrows

reduced
oxidized



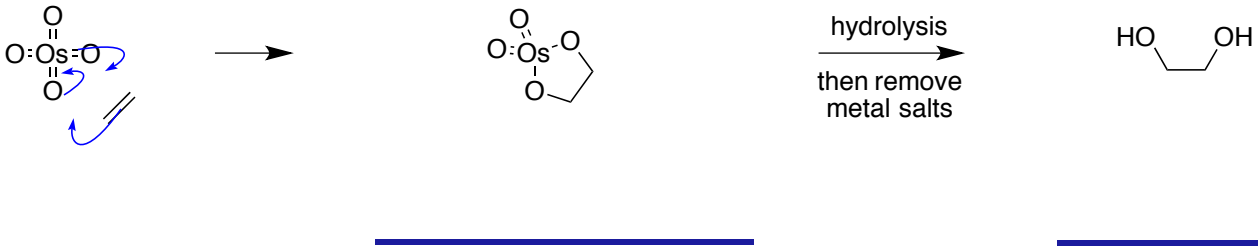

(i) O_3
(ii) PPh_3
O
+
O

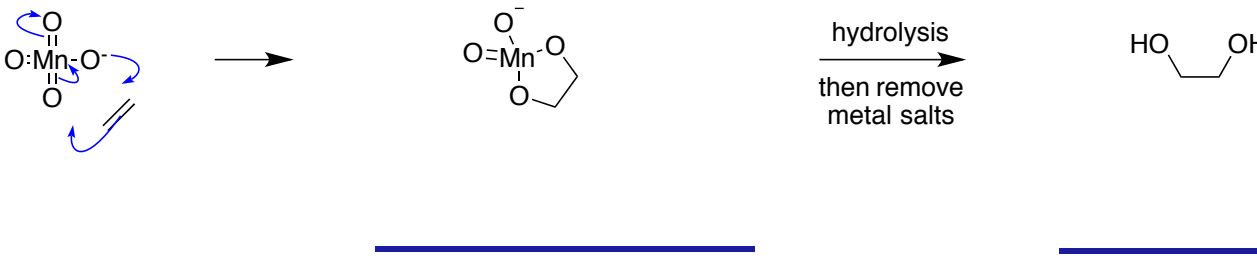

(i) O_3
(ii) $NaBH_4$
HO
OH


(i) O_3
(ii) H_2O_2
O
+
O
OH

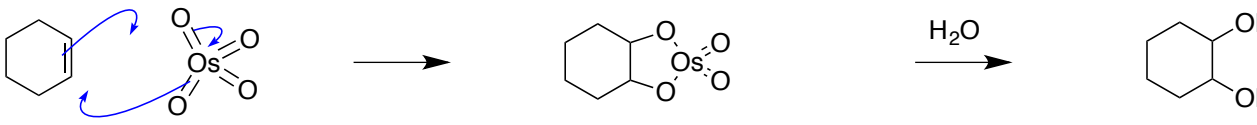
E. Dihydroxylation [2 + 3]

A dihydroxylation adds __2__



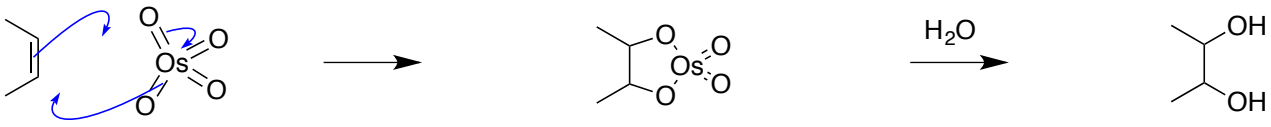


syn face specificity.

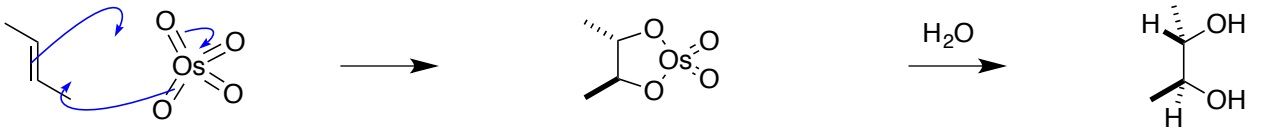


osmate ester

diol

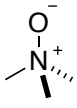


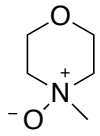
osmate ester *diol*



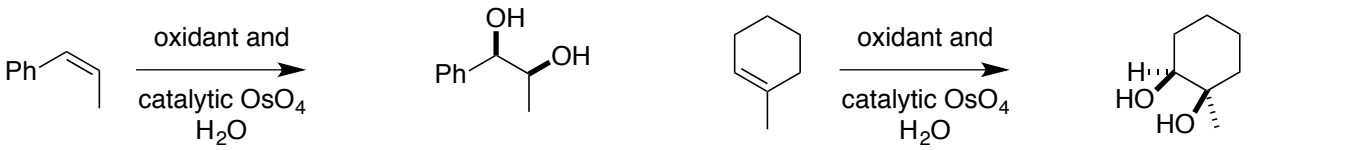
osmate ester *diol*

cis.
This is *unlike*
trans addition of

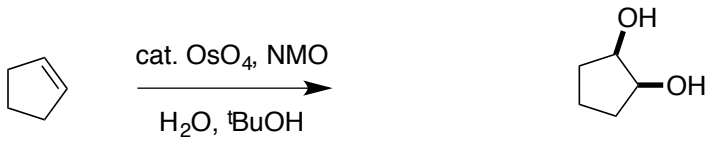


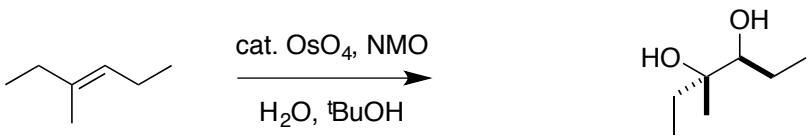


trimethylamine-N-oxide *NMO*



show stereochemistry

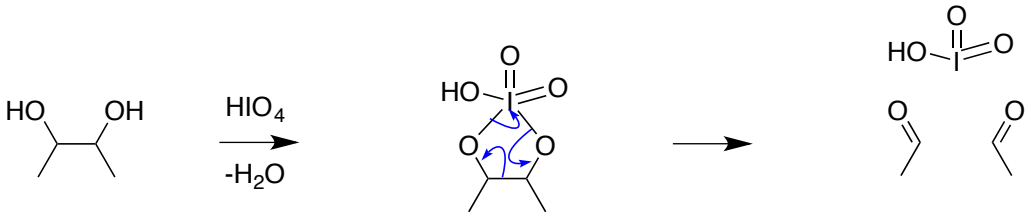


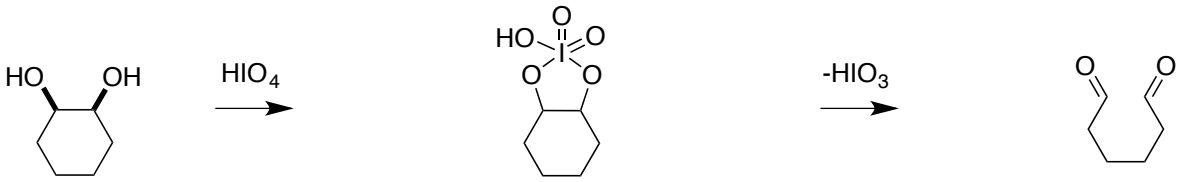


F. Periodate Cleavage

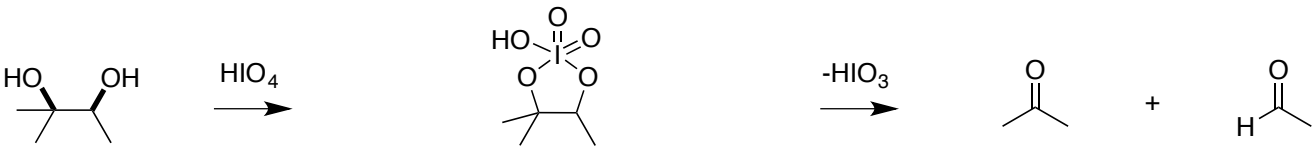
+7 oxidation state; it is reduced

+5





periodate intermediate *products*



periodate intermediate *products*

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

at the end of a chain.

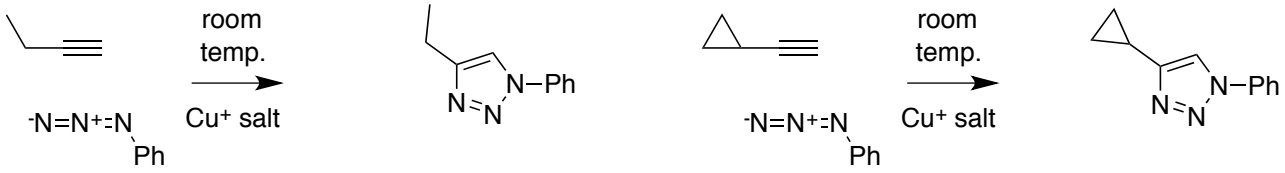
[3 + 2]

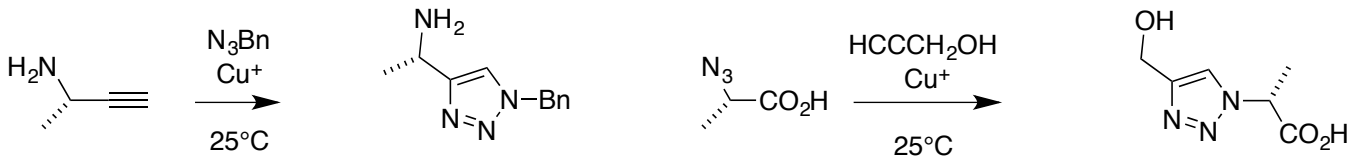
regioisomers

regioselective.

1,4-addition product *1,5-addition product*

chemoselective.

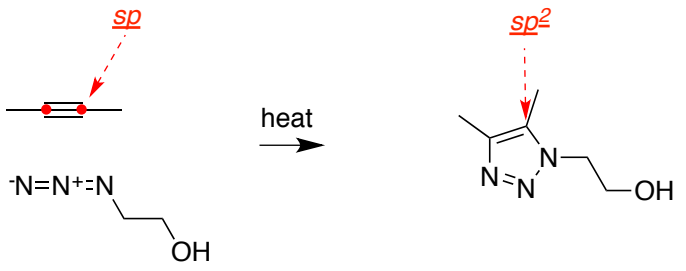




none

chemoselective.

less stable



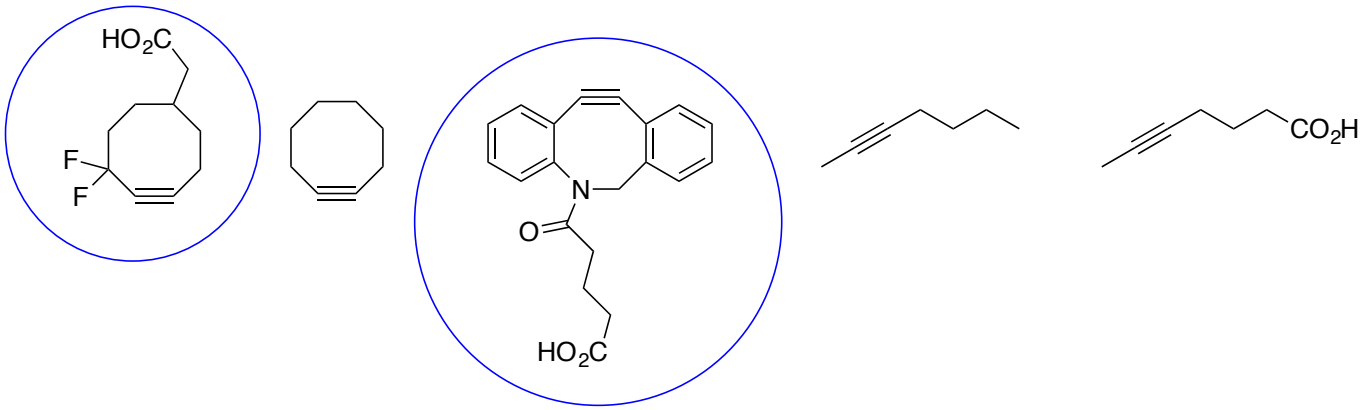
triazole product

180
120°.

cycloheptyne | cyclopropyne | cyclooctyne | cycloundodecyne

3 | 4 | 2 | 1

hydrogenation
most strained, *ie* cyclopropyne
sp^3, thereby making those carbon atoms
sp^2, thereby making those carbon atoms more



can
do not need