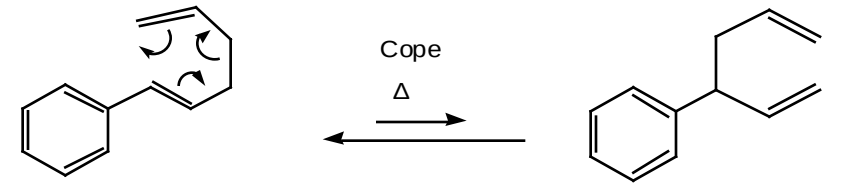
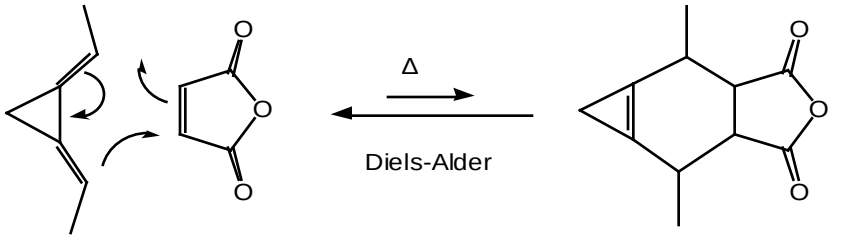
Answers to Hour Examination #1, Chemistry 302X-302A, 2005

1a



Moves a double bond out of conjugation - not favorable. In addition, one double bond is less substituted, and hence, less stable.

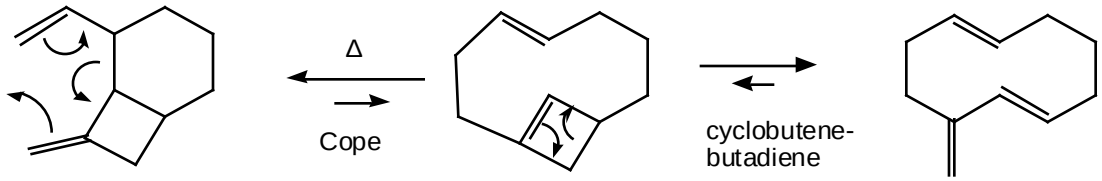
X

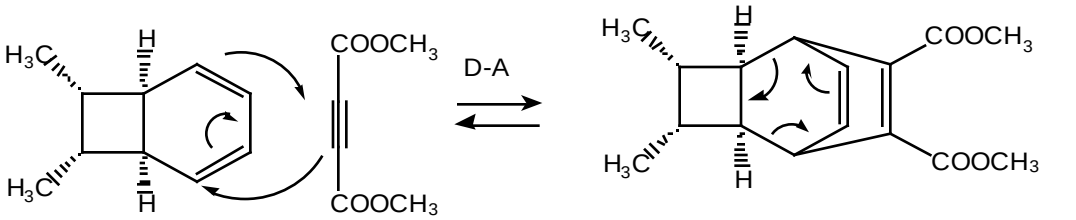


Moves double bond into the three-ring - unfavorable strain

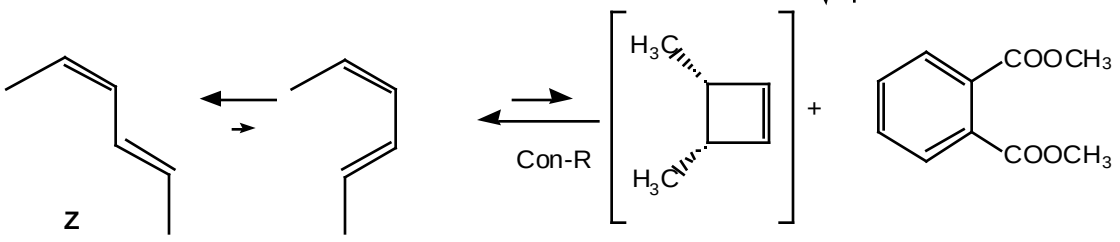
Y

1b



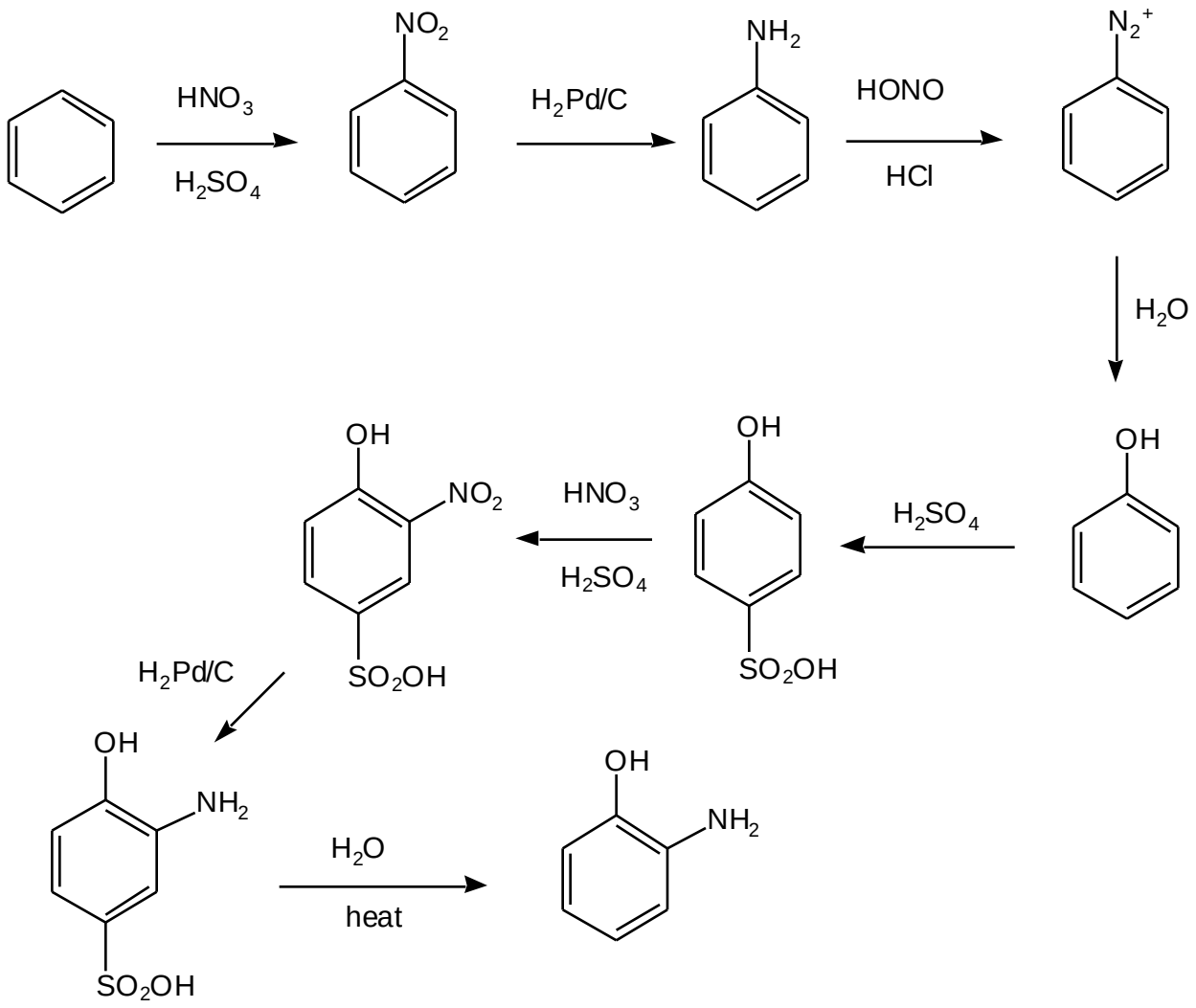


reverse
D-A

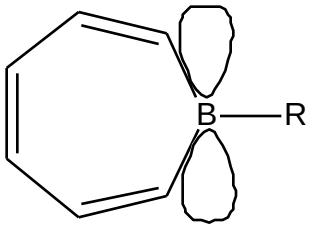


unstable - and can't be **Z**-
too few vinyl hydrogens

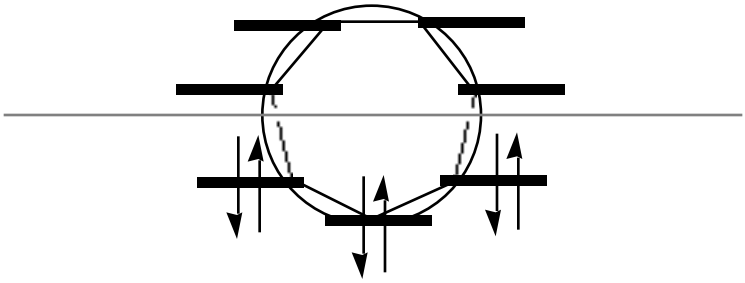
2.


HNO3
H2SO4
NO2
H2Pd/C
NH2
HONO
HCl
N2+
H2O
OH
H2SO4
HNO3
H2SO4
SO2OH
H2Pd/C
NH2
H2O
heat

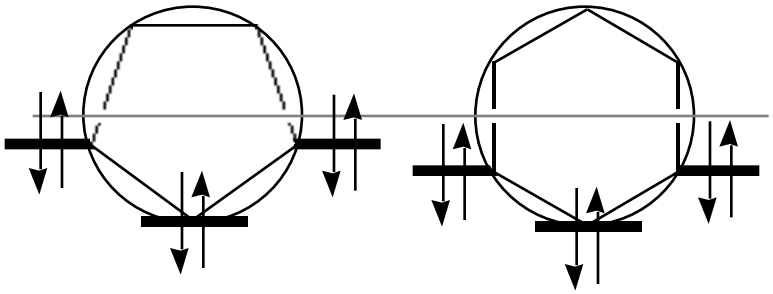
3.
Boron has an empty 2*p* orbital, so borepin is isoelectronic with the tropylium ion.



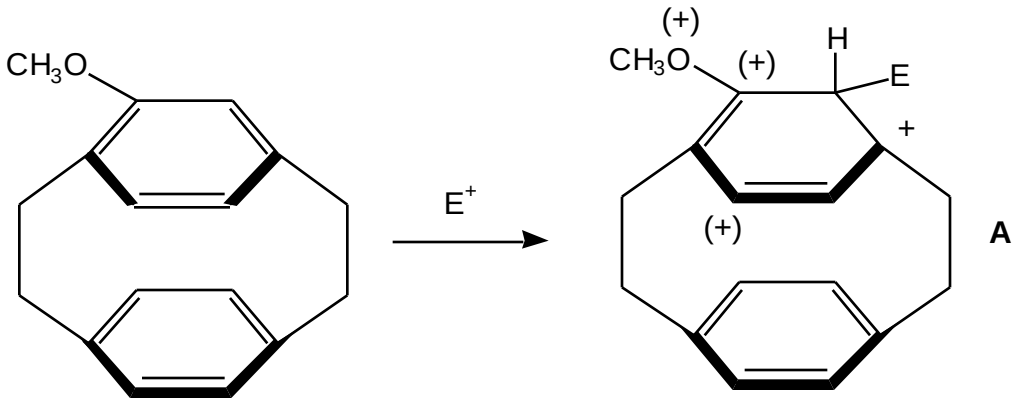
There are six pi electrons (two from each of three double bonds) in a set of fully-filled bonding MO's. There are no electrons in nonbonding or antibonding orbitals. A Frost circle tells the tale:



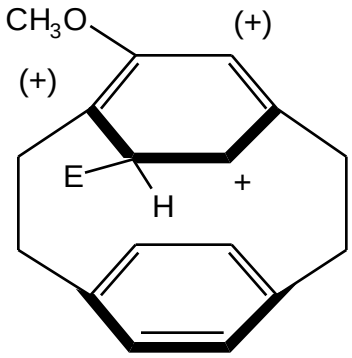
Furan vs. benzene: Look at the electronic occupancy when the polygons are properly inscribed vertex down. The four electrons in the HOMOs are lower in benzene than in furan.



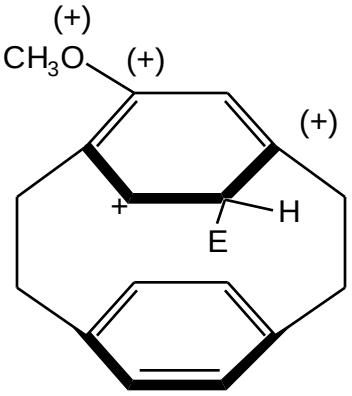
4a. Substitution at two positions (**A** and **B**) allows the methoxy oxygen to stabilize the intermediate, but the third (**C**) does not.



2 **A**

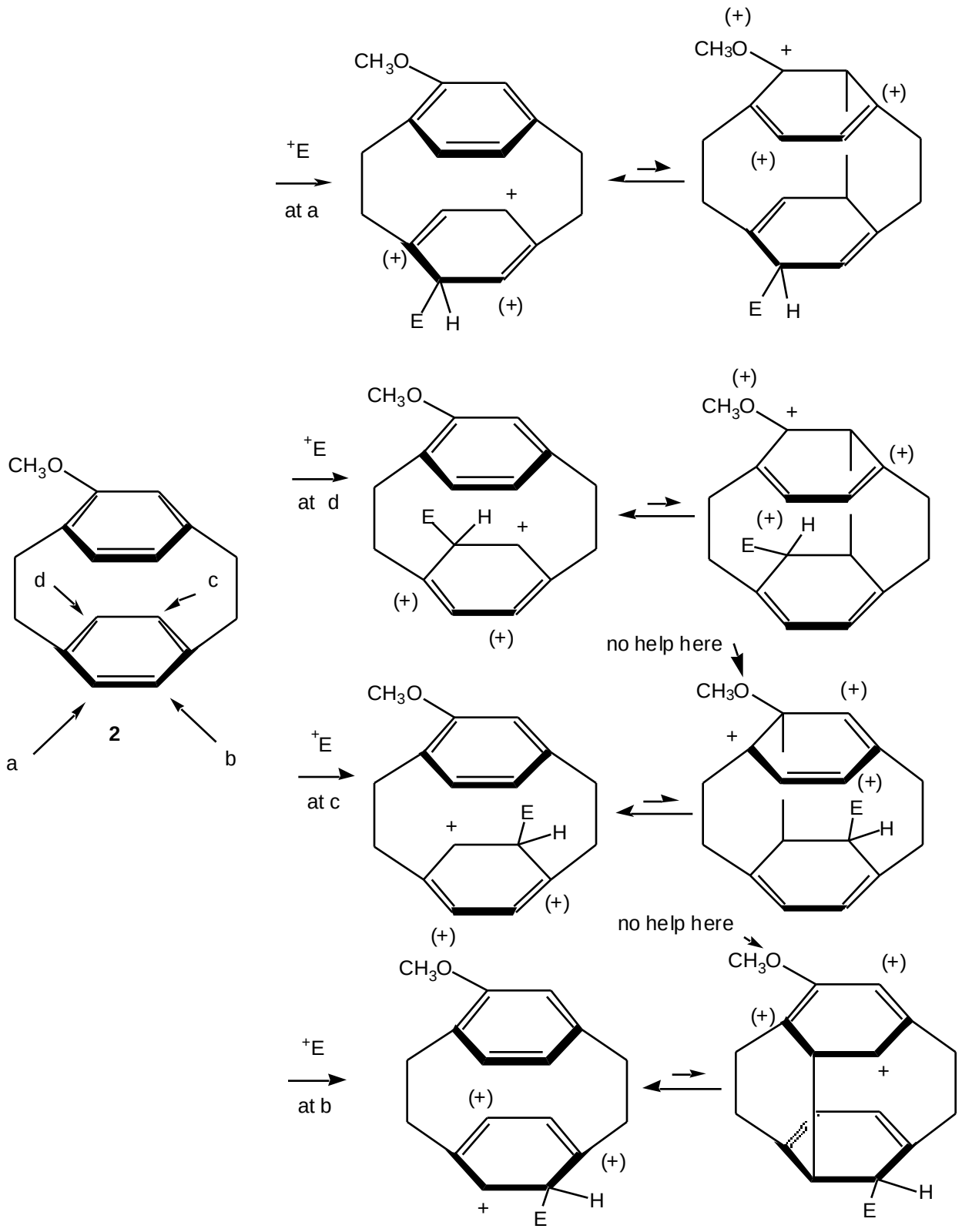


C

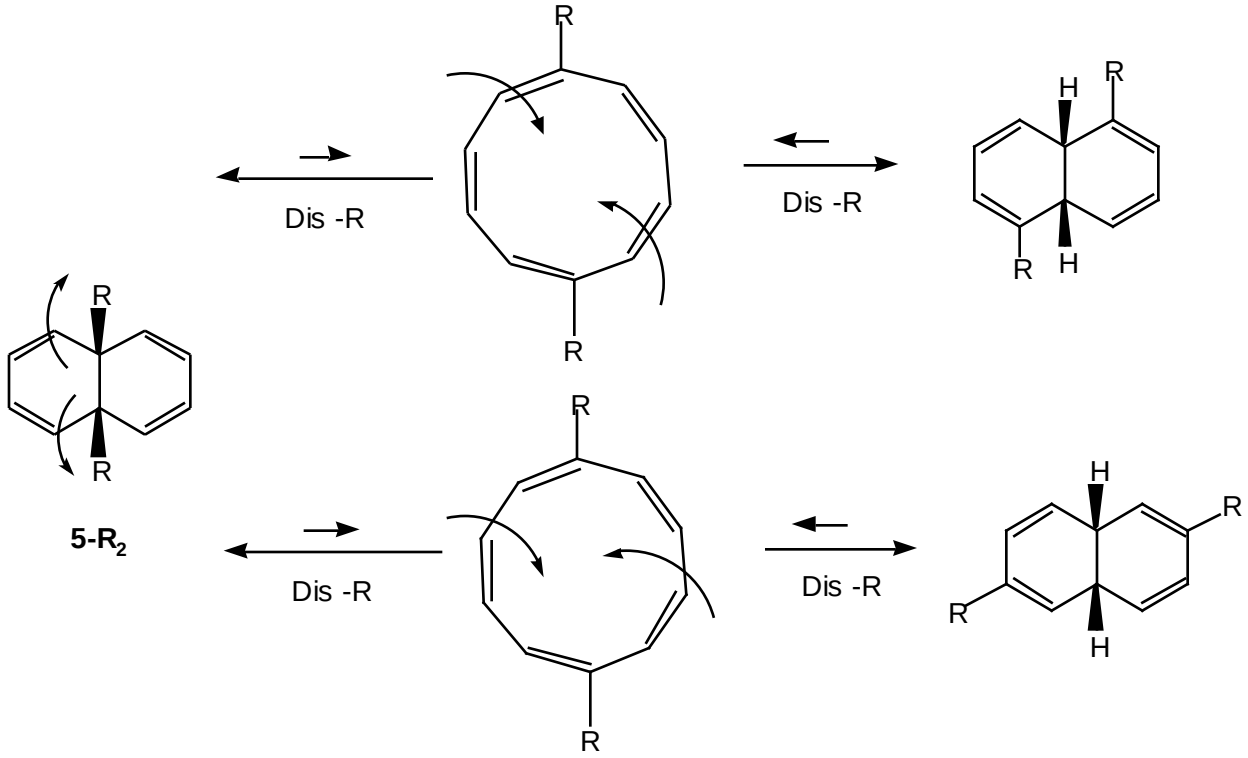


B

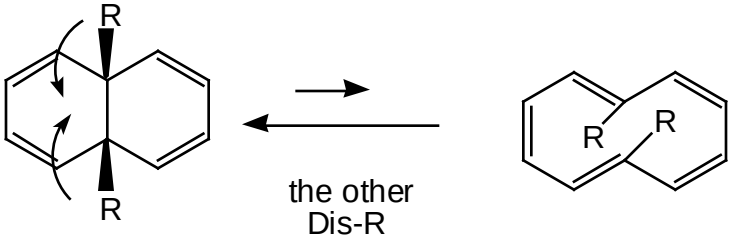
4b. Look at the four possibilities. In each, the top (CH_3O- substituted) ring can help stabilize the positive change. But in only two of those bridged intermediates can the oxygen help out. Those are positions a and d, so substitution is faster there.


CH3O
+E
at a
(+)
+
E
H
at d
at c
at b
no help here
2
a
b
c
d

5a. Compound **5** *is* opening to a ten membered ring, all-*cis*-cyclodecapentaene, but that compound is much too unstable to survive. It re-closes to **5**, but, of course in the labelled molecule there are three ways to do the closure. One simply reverses to **5** but the other two go on to the rearranged products. Note that all motions in these thermal 4n + 2 processes must be dis-rotatory.

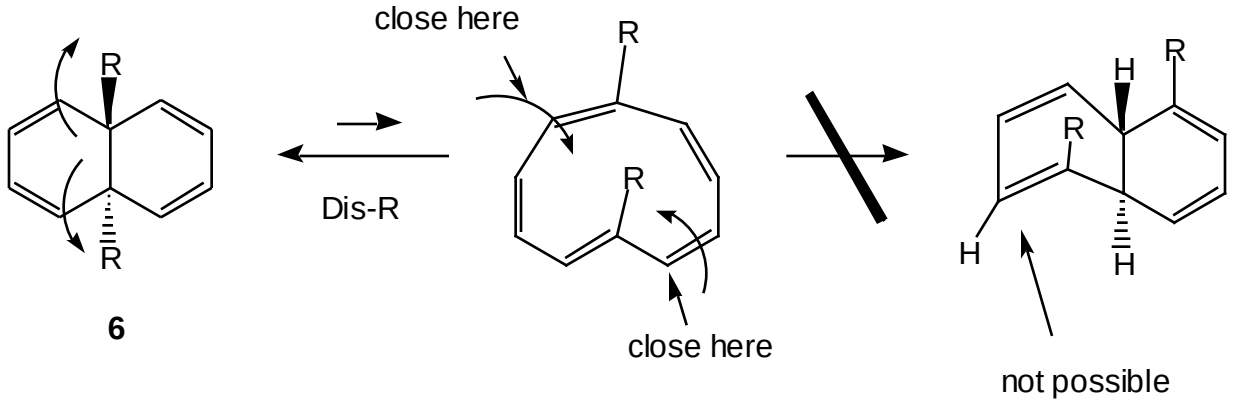


Of course, there is another possible disrotatory opening of **5** that gives the *cis,trans,cis,cis,trans*-cyclodecapentaene. But that molecule (see 5b below) is condemned only to reclose to **5**. It cannot do anything else, as other closures would leave two trans double bonds in six-membered rings (again, see 5b).



very unstable- two
trans double bonds
in the ring, and those
R groups are in the same space

5b. In the trans molecule **6** a disrotatory opening must lead to the cis,cis,cis,cis,trans-cyclodecapentaene. Reclosure must take place so as to get rid of that trans double bond, so there is no way to make “rearranged” products. Other closures would lead to **6** molecules containing a trans double bond in a six-membered ring - no, no, no.



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