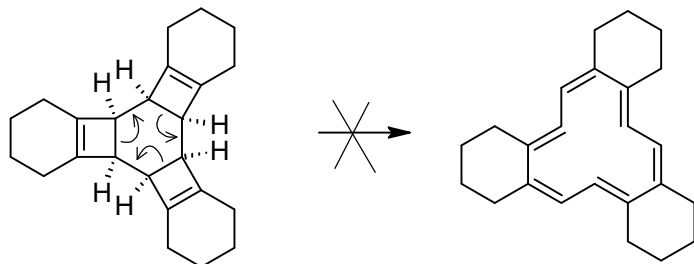
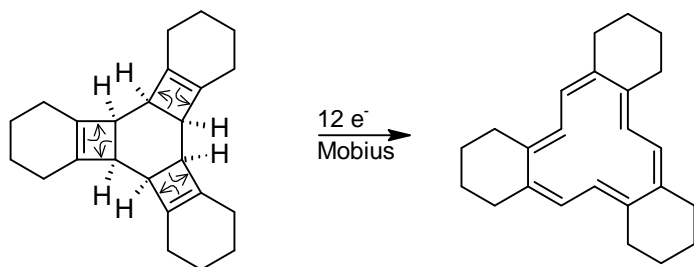


#1

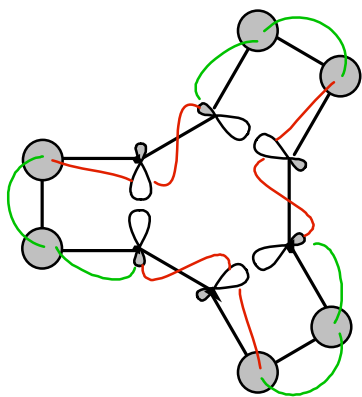
Conversion of 1 to 2



My first and simplest idea is **terribly wrong**. The curved arrows don't put the double bonds where they belong in the product. You should not have considered this possibility.



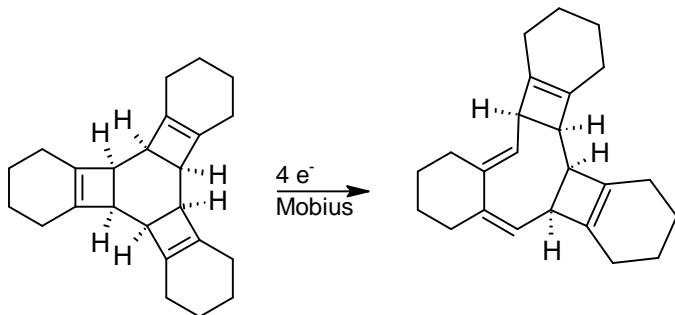
This, on the other hand, is the one-step transformation that you should consider. It puts the double bonds in the right spots. If you compare H positions in **1** and **2**, you can see that all three rings must open in a conrotatory fashion.



The orbital array was an awful thing to draw. To make my life a little simpler, I have drawn only the "front" lobe of each p orbital because that is the only lobe that's needed.

The overlap lines use the lobe of each hybrid orbital that will *end up* pointing forward, towards you, in the product. The red lines show the nodes (antibonding overlaps) and there are 6 of them.

This is a Huckel array so the reaction is forbidden.



This is a standard conrotatory ring opening of cyclobutene like we covered in class. I won't bother drawing the orbital array. The product looks very strained, doesn't it? I haven't tried to build a model ...

The authors believe that this reaction would be followed by two other cyclobutene ring-openings, all 4 electron, all Mobius, all conrotatory. Since the

#1 cont'd

Conversion of 3 to 4

The triene formed by the "top" three alkenes in **3** undergo a 6 electron, Huckel, disrotatory ring-closure.

Conversion of 4 to 6

The triene in **4** undergoes a 6 electron, Huckel, disrotatory ring-closure.

Conversion of 4 to 5

The central alkene in the triene portion of **4** acts like a dienophile and undergoes a 6 electron, 4+2 (Diels-Alder), Huckel, cycloaddition.

#2

Most of these steps are equivalent to reactions in Scheme 1. Thus:

8 to 9 is equivalent to **3 to 4**

9 to 10 is equivalent to **4 to 6**

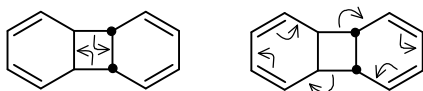
9 to 11 is equivalent to **4 to 5**

A note of interest: the reaction scheme represented by Scheme 2 is actually much more complicated than it first appears. It is also slightly misleading. As the authors reveal (see *Org Lett*, **2008**, *10*(6), 1287), three conformations can be drawn for **8** (**8abc**) and two conformations for **9** (**9-syn** and **9-anti**). There are also two possible stereoisomers for **10**. The one shown in Scheme 2 is **10-anti**, while the other, an *all-cis* stereoisomer, is called **10-syn**.

Here's the misleading part. Scheme 2 suggests that a common intermediate, **9**, can lead to **10-anti** and **11**, but this isn't quite right. As Scheme 3 in the paper shows, one conformer, **9-anti**, can form **10-anti**, but it cannot form **11**. The other conformer, **9-syn**, can form **10-syn** or **11**, but it cannot form **10-anti**. In other words, no single conformer of **9** can form both **10-anti** and **11**. FYI - this ambiguity does not exist in Scheme 1. The fused cyclohexane rings prevent **4** from undergoing conformational changes and **6** is actually analogous to **10-syn**.

Conversion of 10-anti to two benzenes

You can look at this two ways. If you treat the pi electrons as spectators, this is a 4 electron, Huckel, retro-2+2 cycloaddition and is forbidden. On the other hand, if you include the pi electrons, this is a 12 electron system, but the geometry (Huckel) doesn't change and the reaction is still forbidden.

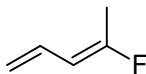


Conversion of tricyclic starting material to 7

If you compare bond positions, the reaction looks quite simple: 4 electron, Huckel, retro-2+2 cycloaddition that is photochemically allowed. This was the answer that I was expecting. However, now that I am looking at this more closely, I see that the retro-2+2 gives a product in which all of the double bonds are *cis* whereas **7** contains alternating *cis* and *trans* double bonds. A one-step mechanism for formation of **7** would seem to be ruled out and I have marked all plausible answers as correct.

#3

a. The HF/3-21G energies of the two transition states are -291.095291 (F rotates in) and -291.113967 au (F rotates out), respectively. That means $\Delta(\Delta E^*)$ is 11.7 kcal/mol. Since the lower barrier is for F rotates out, the kinetic product is:



b. The HF/3-21G energy of the X = F reactant is -291.178343 au. The calculated barriers are 52.1 (F in) and 40.4 (F out) kcal/mol, respectively.

Considering X = H, the HF/3-21G energies of the reactant, H rotates in, and H rotates out transition states are respectively, -192.853174, -192.788042, and -192.777737 au. These values yield barriers of 40.9 (H in) and 47.3 (H out) kcal/mol. F has two different effects on the energy barrier. F raises the barrier by 11 kcal/mol when it rotates in, and it lowers the barrier by 7 kcal/mol when it rotates out.

c. A methyl group should experience greater steric repulsion when it rotates inward. Space-filling models of F and CH₃ show that the latter is indeed larger.

Another way to estimate steric repulsion created when X rotates inward is to compare the X-C-C=C dihedral angles in the two transition states. As X rotates inward, the angle falls to 0° in the product, but it is still much larger in the transition state. The dihedral angle is 67° for X = F (F rotates in), but is 73° for X = CH₃ (CH₃ rotates in). The latter is larger perhaps because CH₃ experiences more steric repulsion.