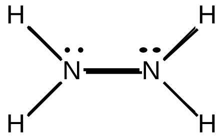
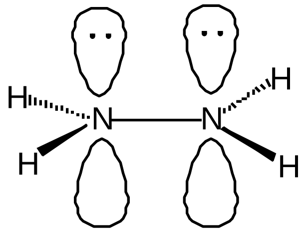
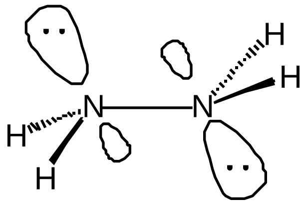
Answers to Hour Examination #1, Chemistry 301/301X - 2004

1a.



b

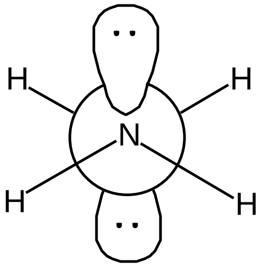


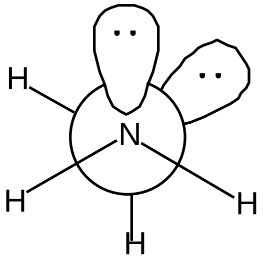


i

ii

iii

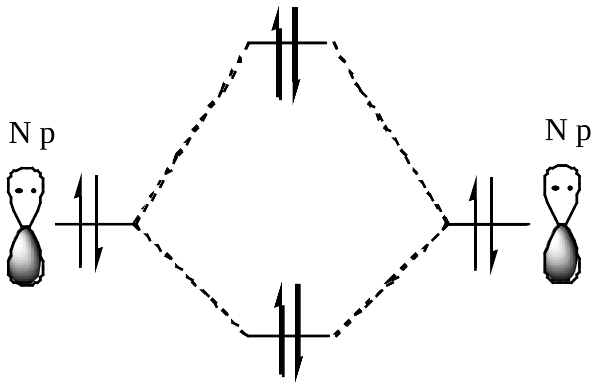


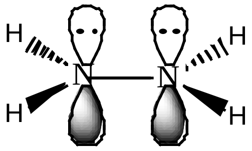


anti

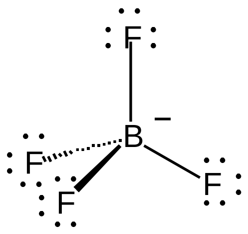
gauche

c. A planar hydrazine would require *sp*^{2} nitrogens. Their lone pairs would reside in aligned *p*-orbitals, which is energetically destabilizing as electrons are forced into antibonding orbitals.

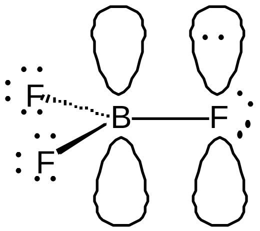




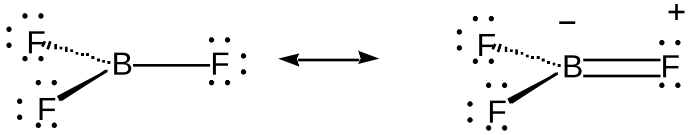
2a,b.



B is sp^3

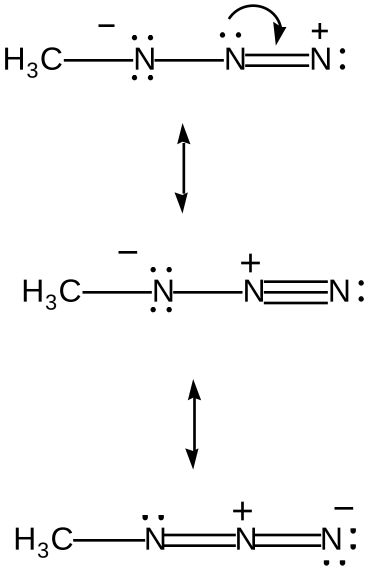


B is sp^2



The sp^2 bonds emanating from boron in BF_3 contain more *s* character than do the sp^3 bonds in $^-BF_4$ and thus form correspondingly shorter sigma bonds with fluorine. Furthermore, and most importantly, the empty *p* orbital on boron in BF_3 can accept electron density from neighboring fluorines (overlapping 2*p* orbitals), leading to resonance structures with double bond character in each of the B—F bonds, thus shortening the bond distance between them.

c. Two possible answers:



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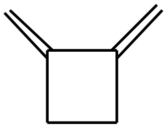
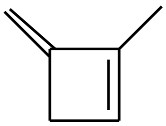
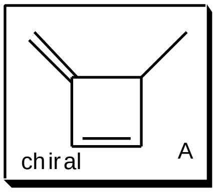
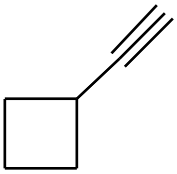
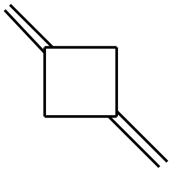
3.

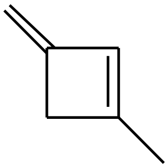


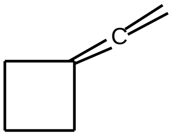


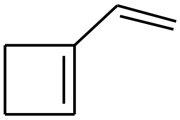


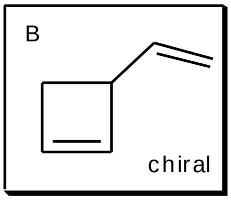


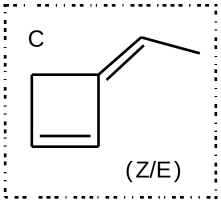




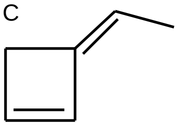




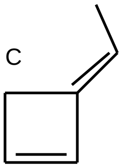




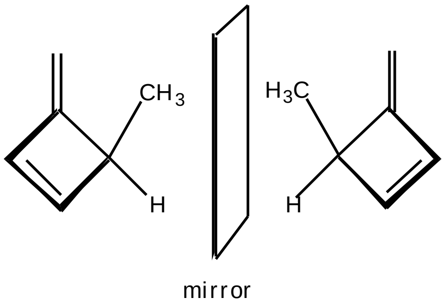
C



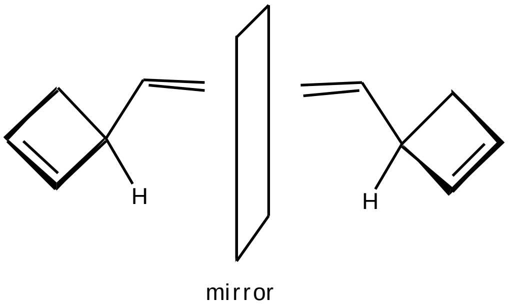
C

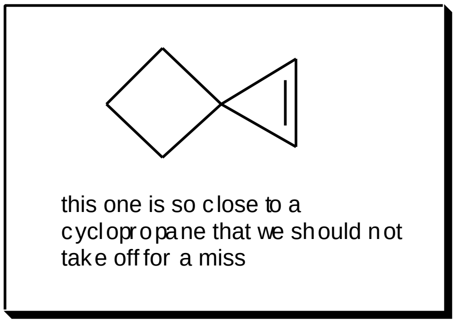


A



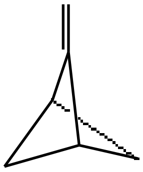
B

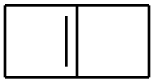


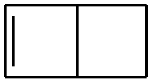


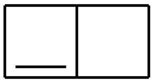
this one is so close to a cyclopropane that we should not take off for a miss

more than one four-membered ring:





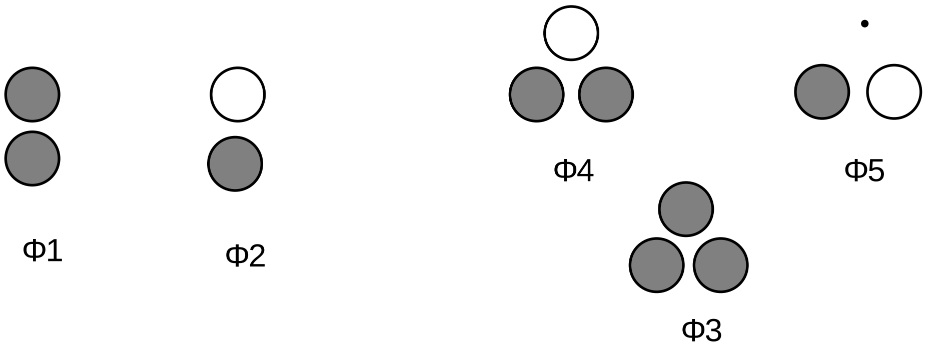




4.

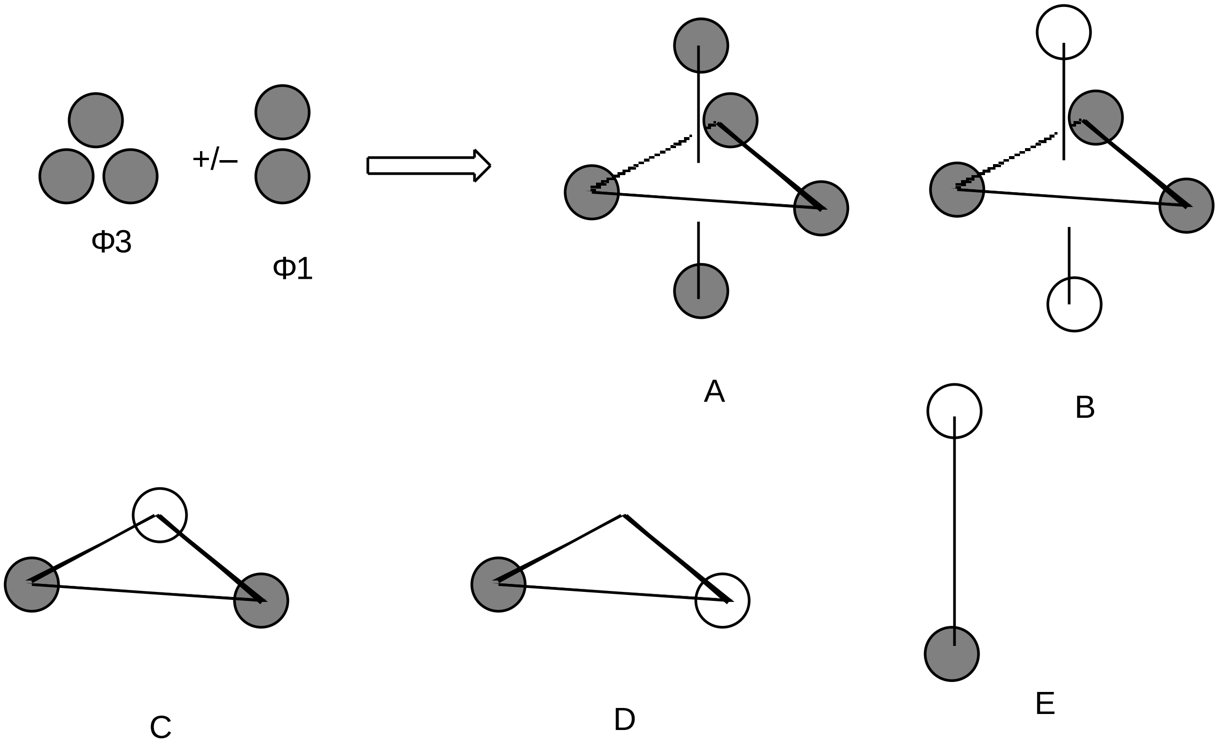
a. These MO's are H_2 bonding and antibonding (Φ1,Φ2) and the three MO's of cyclic

H_3 (Φ3, Φ4, Φ5):



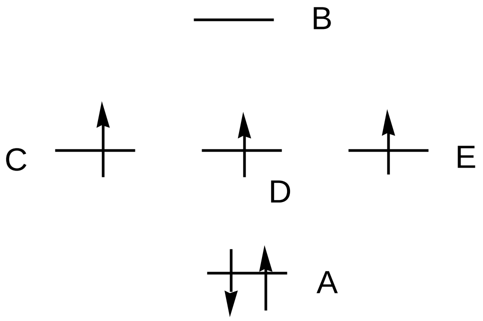
b. H_5 must have 5 MO’s, as it is constructed from five H 1*s* orbitals, or five MO’s..

c. Only the lowest of the cyclic H_3 orbitals (Φ3) can interact with the lower MO of H_2 (Φ1). This interaction produces two new MO’s (A and B). All other potential interactions involve orthogonal, “net-zero” interactions. Thus, the remaining three orbitals; two from cyclic H_3 (Φ4 and Φ5) and the antibonding orbital of H_2 (Φ2) make up the other three MO’s of H_5 (C, D, E).

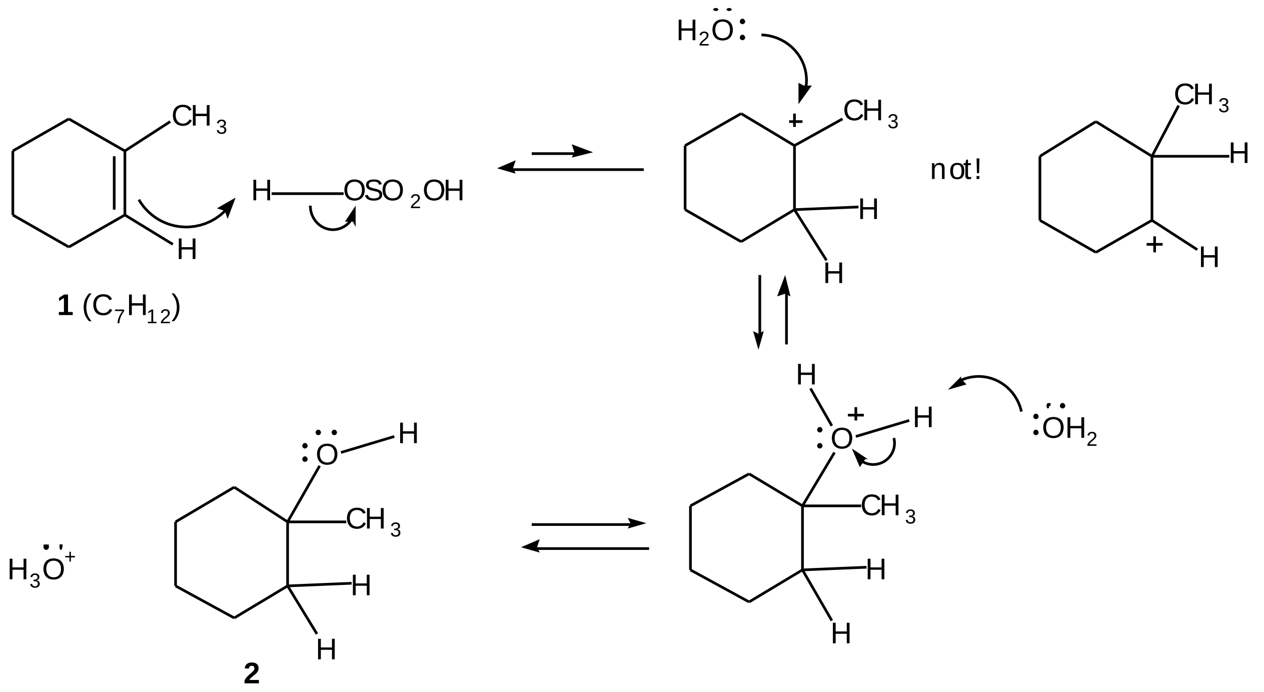


d. Assume MO’s with equal numbers of nodes have equal energy.

e. Five electrons go in as shown, obeying Hund's rule.



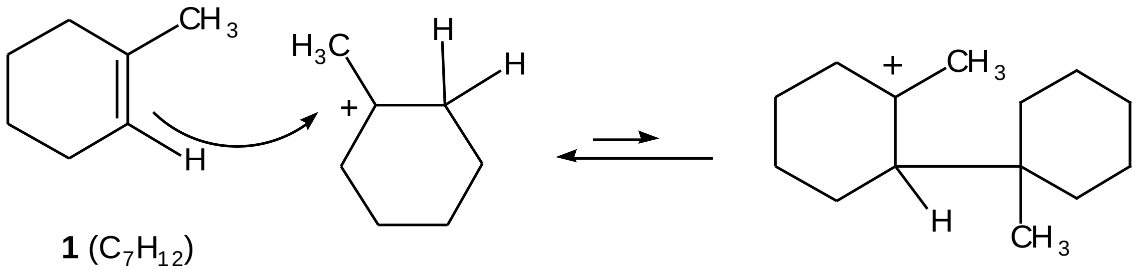
5a.



1 (C_7H_{12})

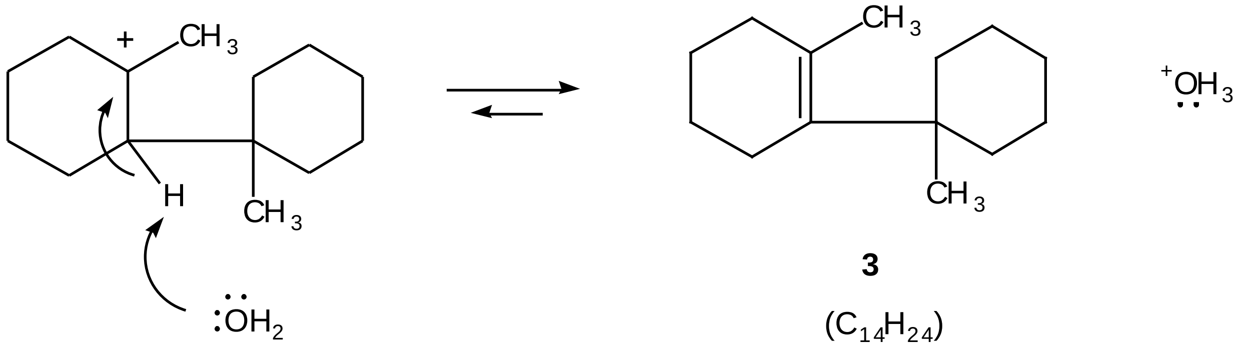
2

5b.When the concentration of water goes down, it becomes less able to add to the tertiary carbocation intermediate (there simply is less of it). Other Lewis bases begin to compete with water for the cation. Other Lewis bases? What can that be? It is right there in front of you - the pi electrons of the alkene acting as Lewis (Brønsted) base in step one. By the way, you knew that something was bringing two of those starting alkenes together, because the formula goes from C_7 to C_{14}. So the first step is:



1 (C_7H_{12})

We are now on proton “high” - this cation is deprotonated to give the most stable possible alkene - the tetrasubstituted **3**. We will hear more about this reaction later.



3

($C_{14}H_{24}$)