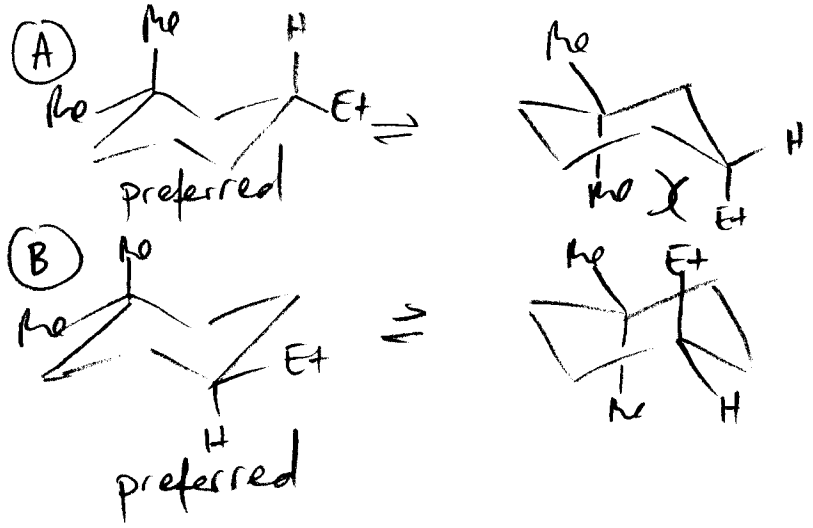
5.12 Review #2 : Solutions

1. 

(A) would have the largest conformational preference because of the destabilizing 1,3-diaxial interaction between methyl & ethyl in the high energy conformer that is not present in (B).

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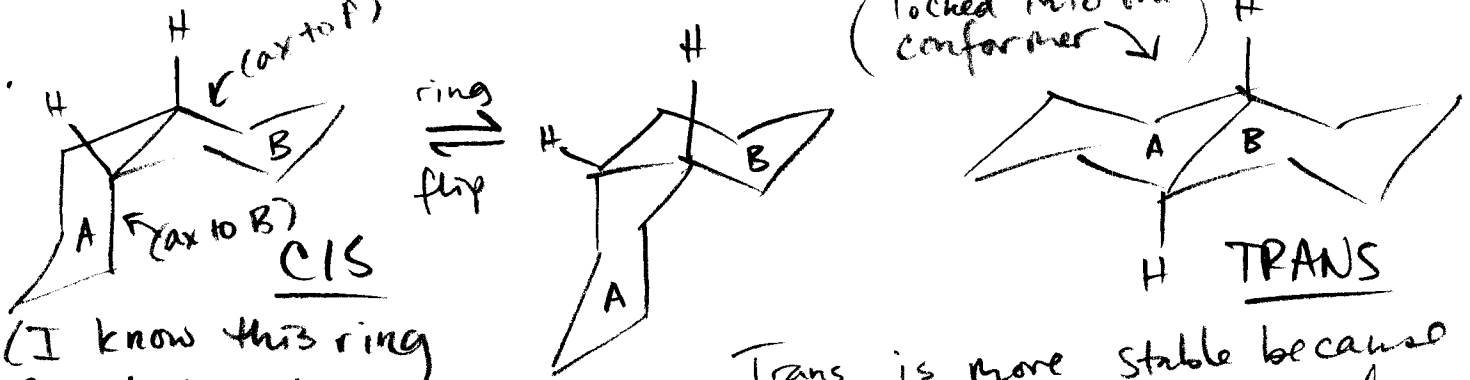
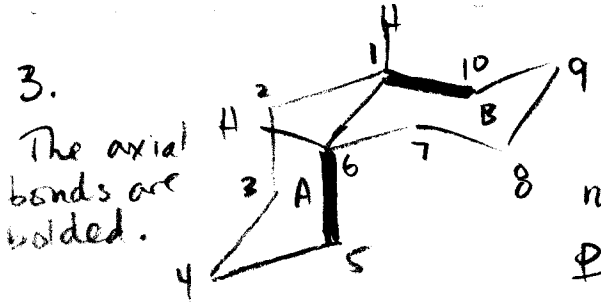
2. 

(I know this ring flip looks strange. Focus on one since they have the same energy.)

Trans is more stable because each ring (A & B) has only equatorial bonds coming off of it. In cis-decalin, each ring (A & B) has one axial & one equatorial bond (see #3).

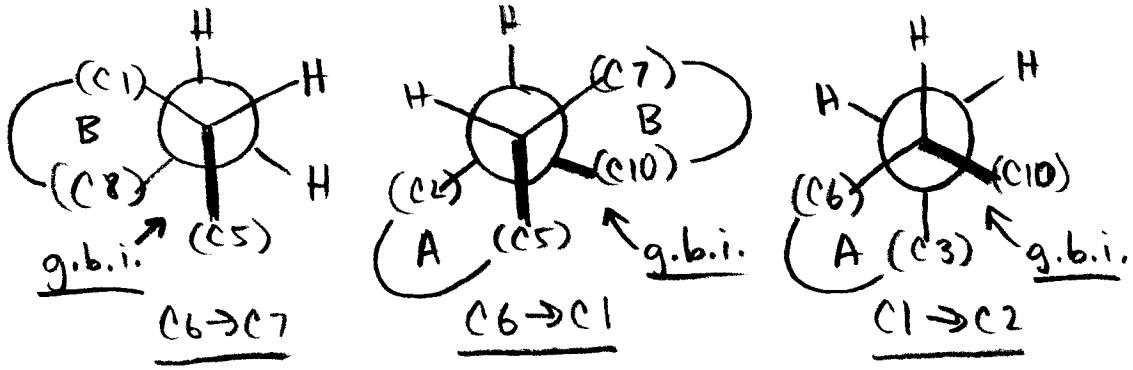
3. 

The axial bonds are bolded.

Cis-decalin has 3 g.b.i.s that are not present in trans-decalin.

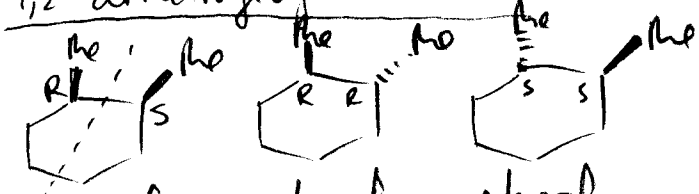
predict: Erel = 3 × 0.9 = 2.7 kcal/mol

(experimental: Erel = 2.8 kcal/mol!)



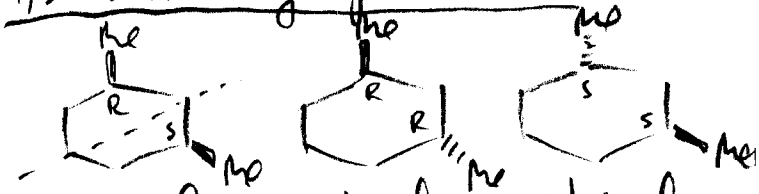
Build models to help you!

1. 1,2-dimethylcyclohexane



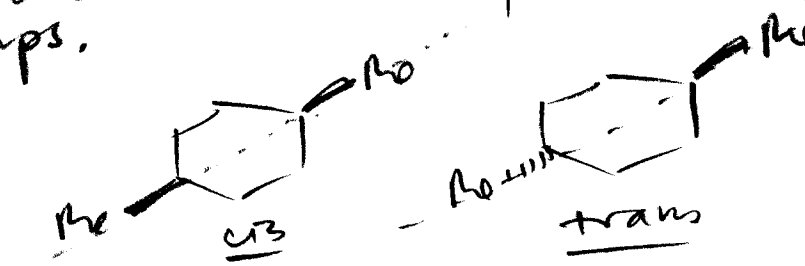
achiral (meso) chiral chiral

1,3-dimethylcyclohexane:



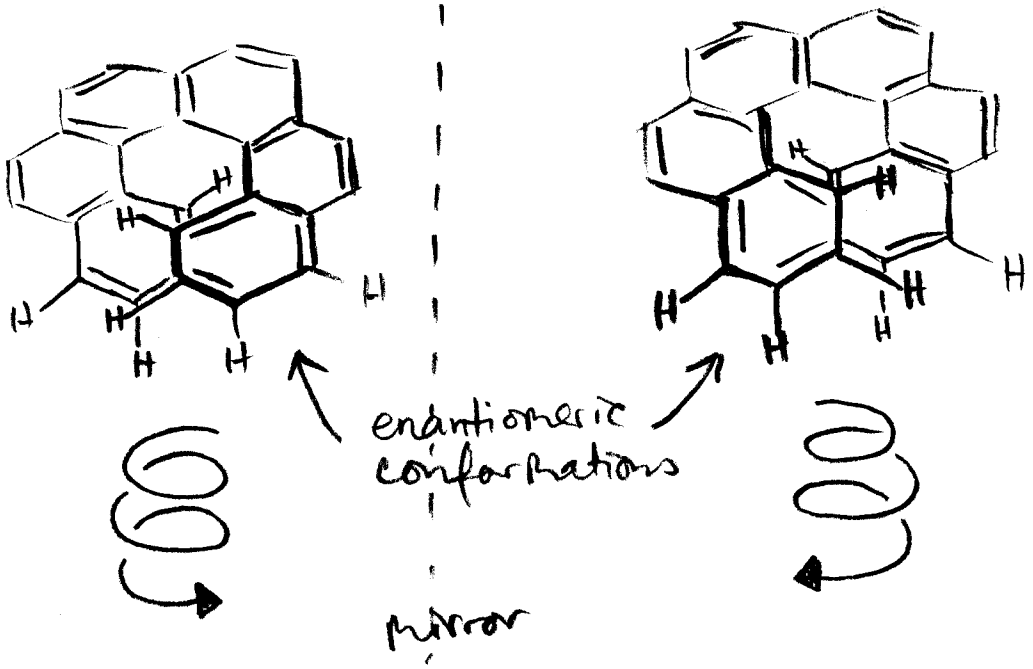
achiral (meso) chiral chiral

Both stereoisomers of 1,4-dimethylcyclohexane are achiral because you can draw a mirror plane that goes through both methyl groups.



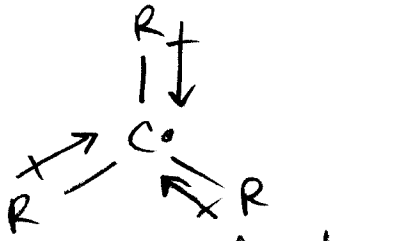
2. You know what to do...

3. Hexahelicene cannot be planar because the two terminal rings would occupy some of the same space. As a result, there are two enantiomeric helical conformations that cannot interconvert.

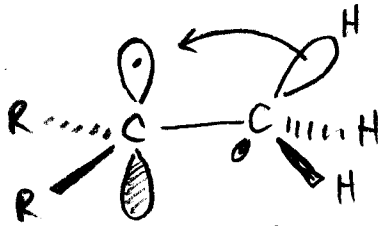


Build a model if it helps!

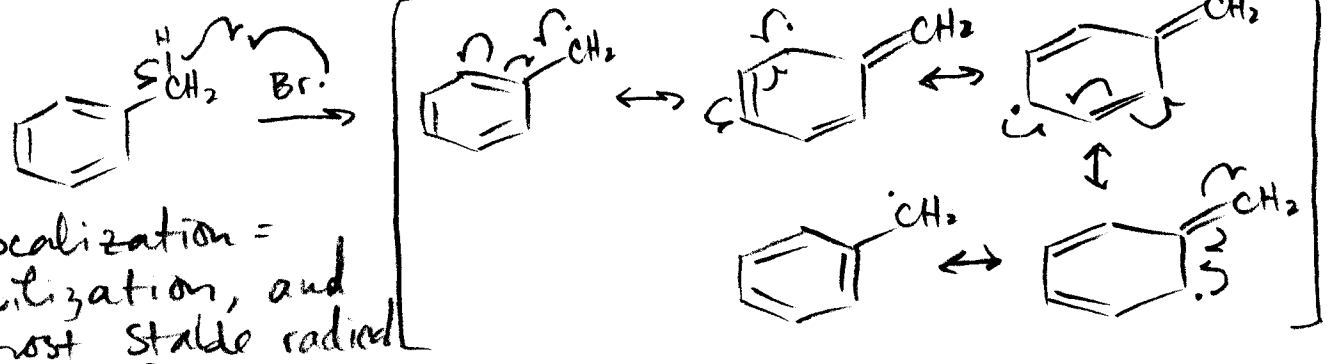
1. Radicals are electron-deficient & alkyl groups can dote electron density in two ways:



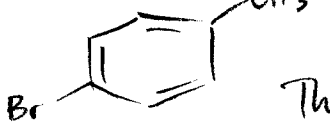
inductive donation



hyperconjugation ($\sigma_{CH} \rightarrow p_c$)

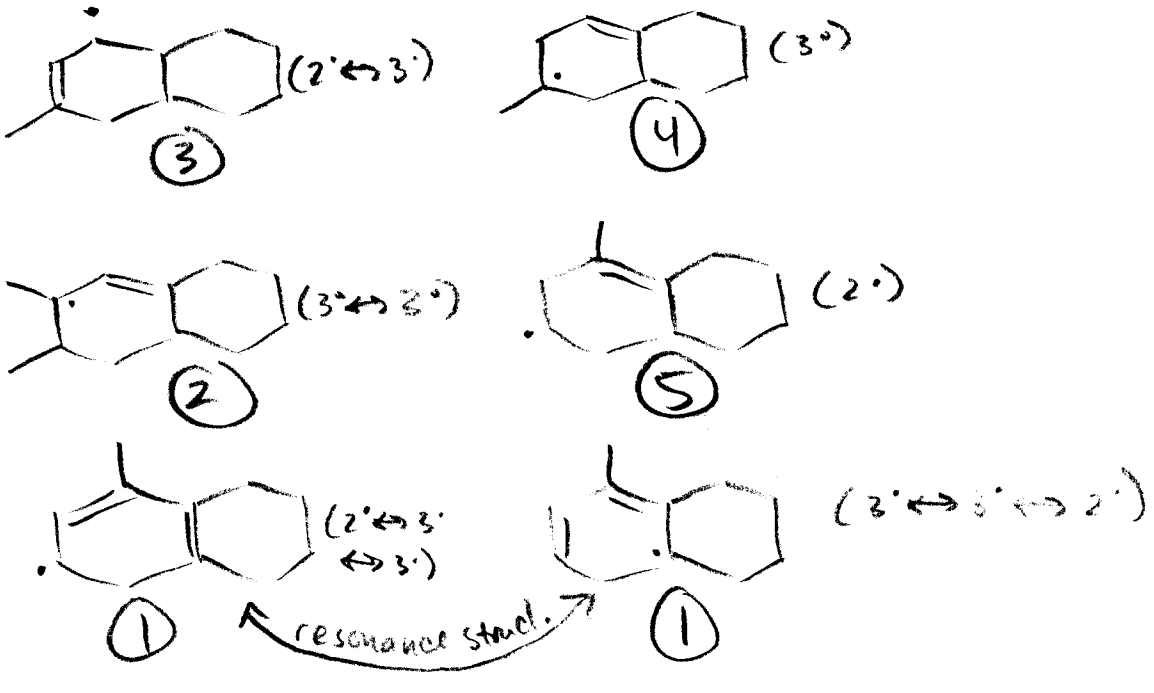
2. 

Delocalization = stabilization, and the most stable radical will form fastest

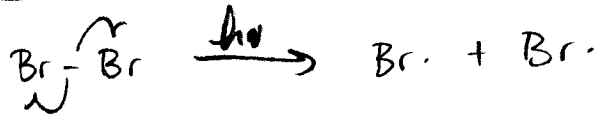


This product would have to result from formation of an sp^2 ("vinyl") radical. This is bad because sp^2 orbitals are more electronegative than sp^3; much less happy to have less than an octet!

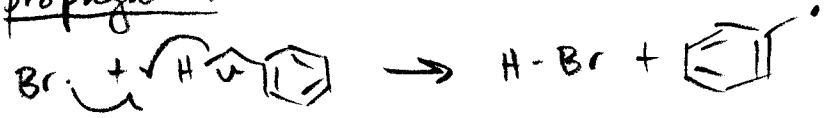
3. On the next page...

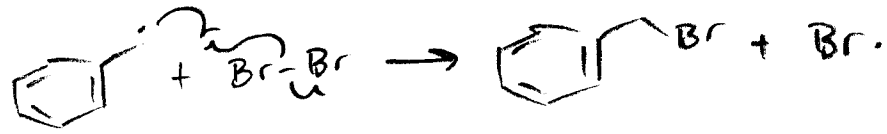
4. 

3. initiation:

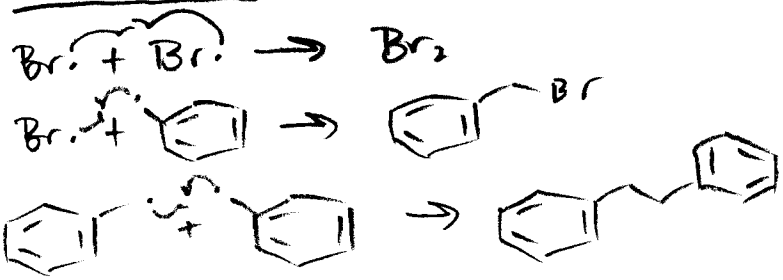


propagation:

#1 

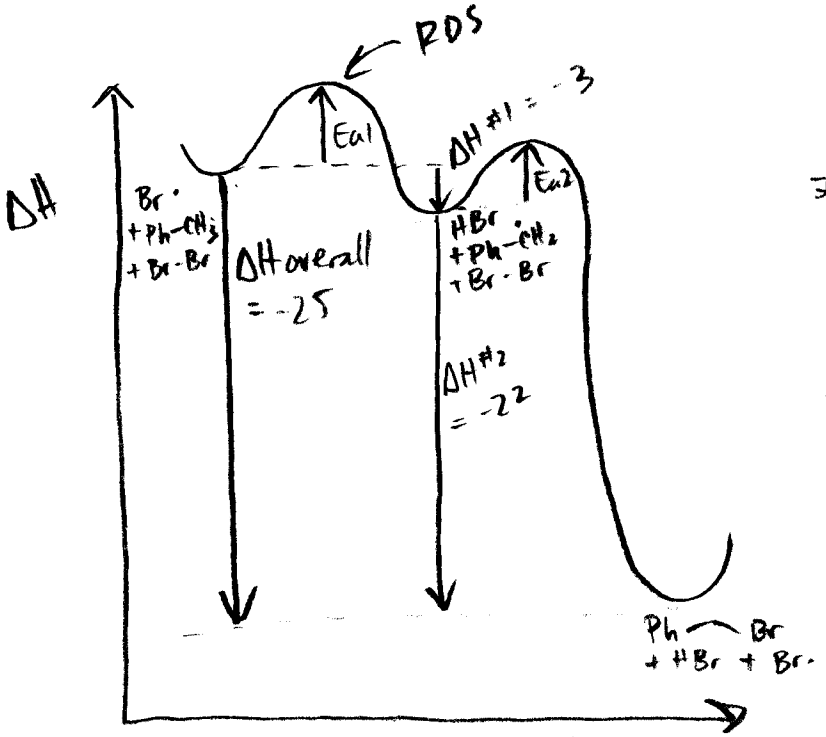
#2 

termination:



#1 make H-Br −88
break benz. C-H +85
ΔH #1 = −3 kcal/mol

#2 make benz. C-Br −68
break Br-Br +46
ΔH #2 = −22 kcal/mol



* make sure you always label your rxn-energy diagrams very thoroughly!