

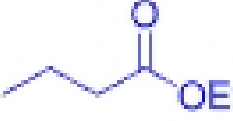
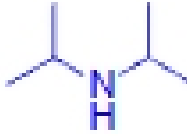



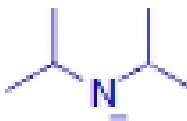
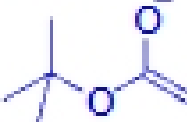

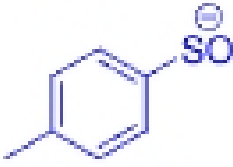
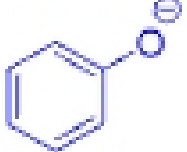


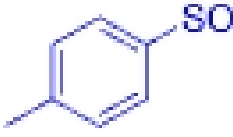
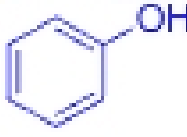


CHEM 348 Test 2 Key – Spring 2010 – 100 points possible

1)

acid	<p><i>iso</i>-Butyl alcohol pKa <u>15</u></p> 	<p>Cyclopentadiene pKa <u>15</u></p> 	<p>Ethylbutanoate pKa <u>25</u></p> 	<p>Diisopropyl amine pKa <u>35</u></p> 
Conjugate base	<p><i>iso</i>-Butoxide anion</p> 	<p>Cyclopentadienide anion</p> 	<p>Ethylbutanoate enolate anion</p> 	<p>Diisopropyl amide anion</p> 

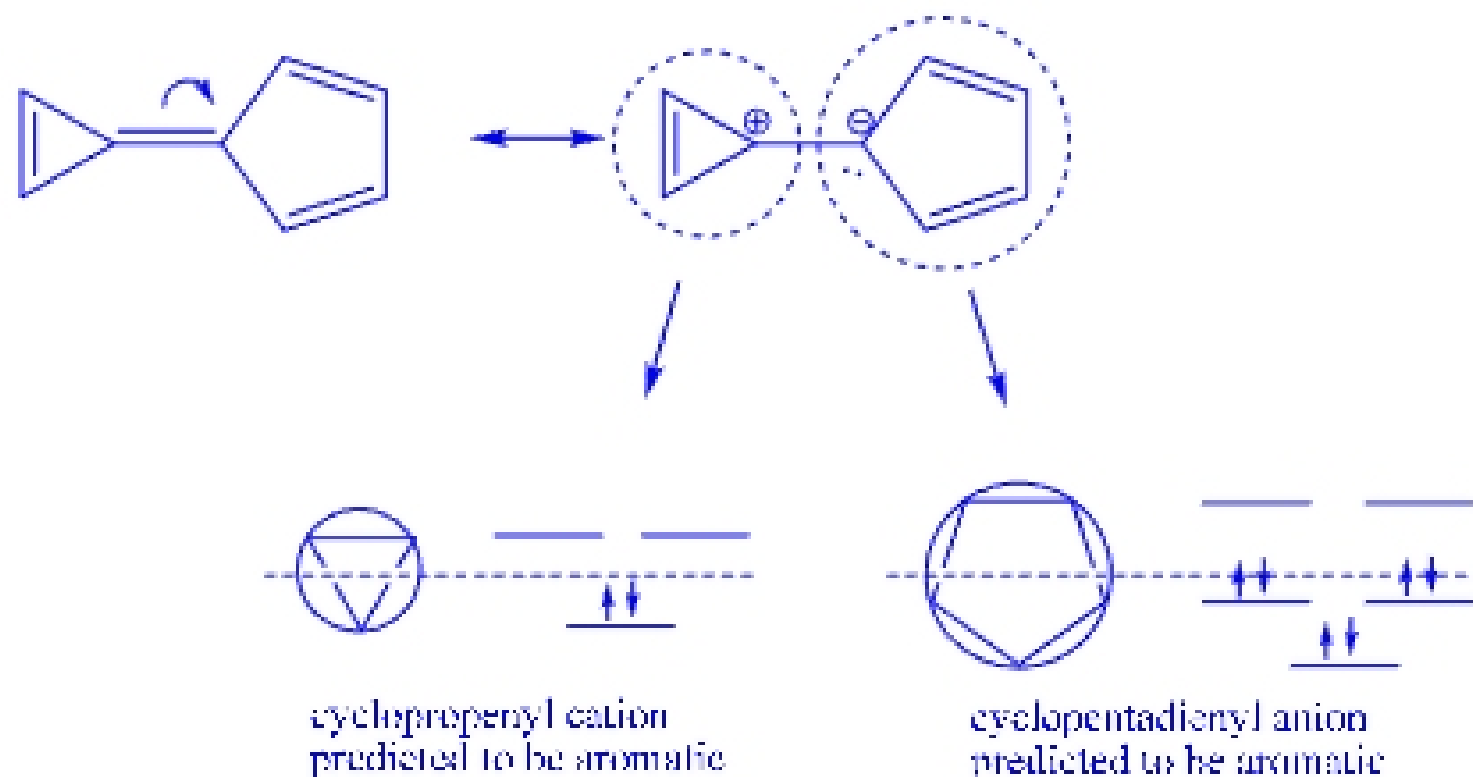
2)

base	<p><i>t</i>-Butyl acetate enolate anion</p> 	<p>Imidazole</p> 	<p><i>p</i>-Toluenesulfonate anion</p> 	<p>Phenoxide anion</p> 
Conjugate acid	<p>pKa <u>25</u> <i>t</i>-Butyl acetate</p> 	<p>pKa <u>5</u> Imidazolium cation</p> 	<p>pKa <u><0</u></p> 	<p>pKa <u>10</u></p> 

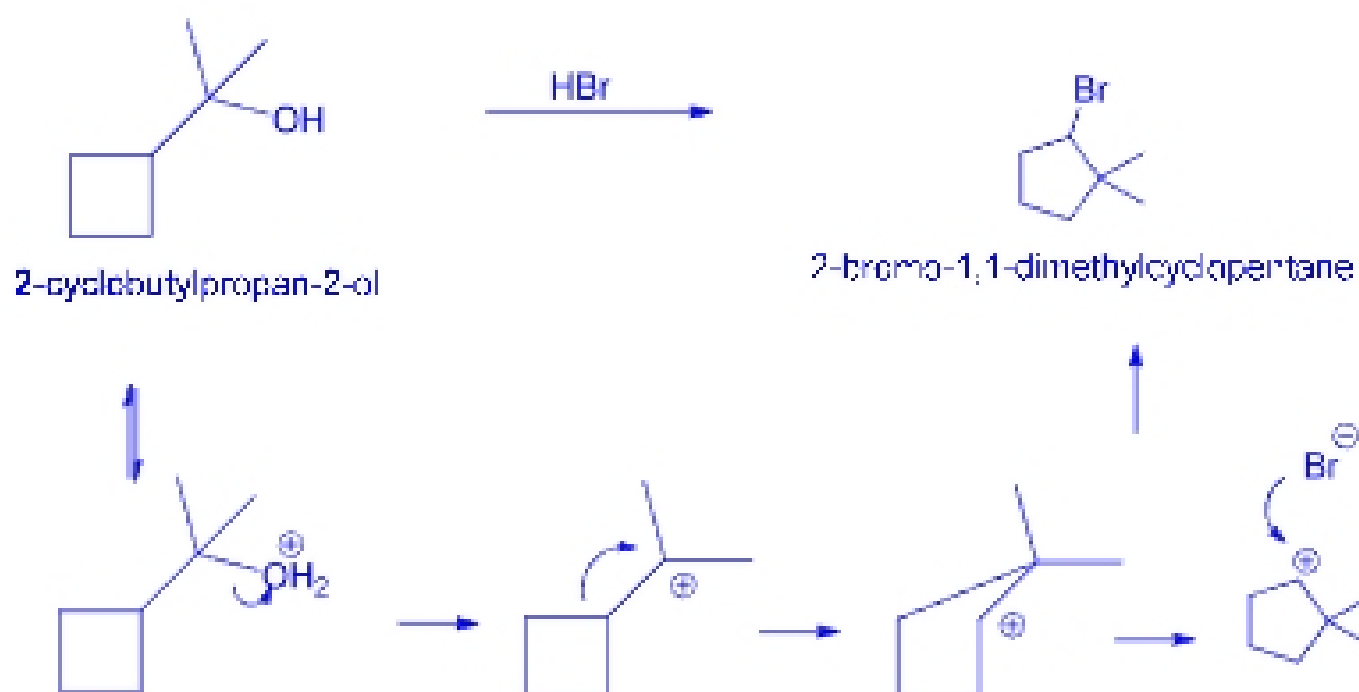
32 points possible

3) The barrier to rotation for compound **1** about the indicated C-C bond is about 65 kcal/mol. Compound **2** (called calicene) has not been synthesized, but computational methods agree the inter-ring rotation should be about 32 kcal/mol. Using good molecular orbital arguments, **explain** using words and pictures why calicene (**2**) has much lower predicted barrier to rotation about the indicated C-C bond.

In the calicene system, an alternate Lewis structure is shown below where the inter-ring double bond is broken in favor of a charge separated species. If you consider each ring independently and use Frost circles, you can justify this resonance form as significant because each ring attains aromaticity.



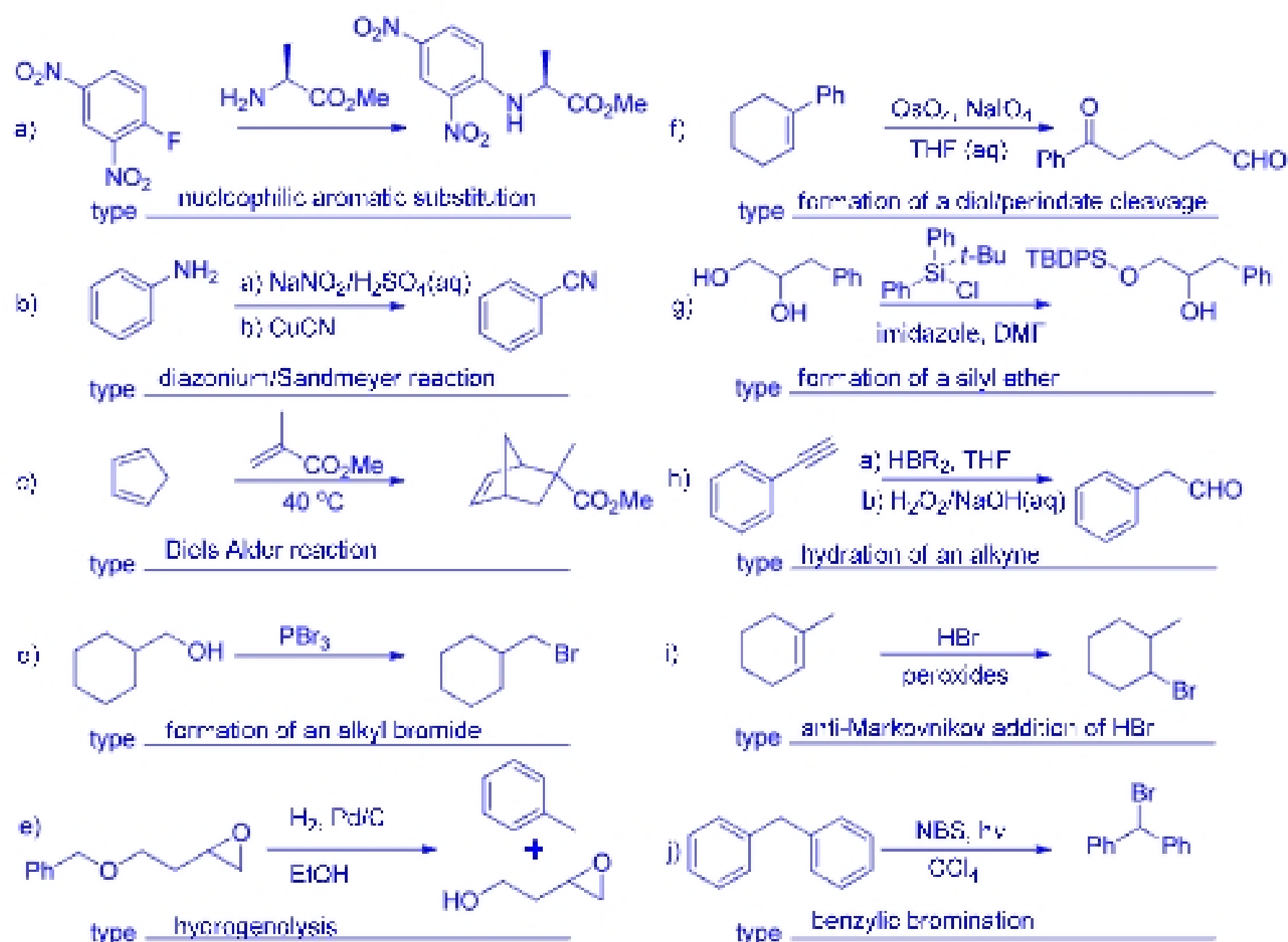
4) When 2-cyclobutylpropan-2-ol is treated with a solution of HBr in Et₂O, 2-bromo-1,1-dimethylcyclopentane is the resulting product. Write the reaction and propose a mechanism using curved arrows notation in each step.



Even though a 3° carbocation is formed, the driving force of this reaction is ring strain

10 points each

5)



28 points possible

6) Propose a synthesis of (*E*)-5-heptene-2-ol using precursors that contain fewer than four (< 4) carbon atoms. Use any necessary organic or inorganic reagents; any reagents or precursors used may contain more than four carbon atoms if fewer than four of the carbon atoms from that reagent or precursor remain in your final product.

10 points possible