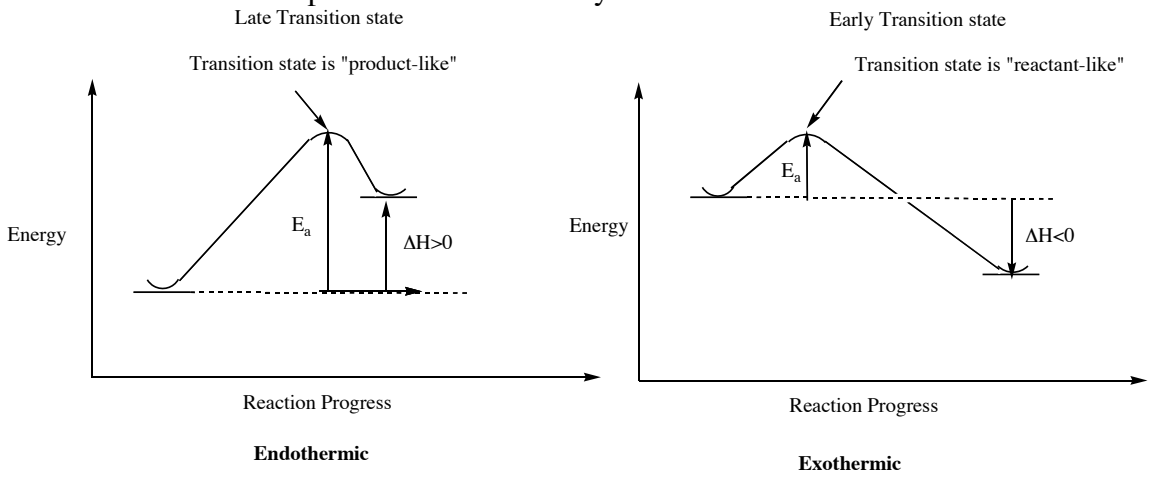
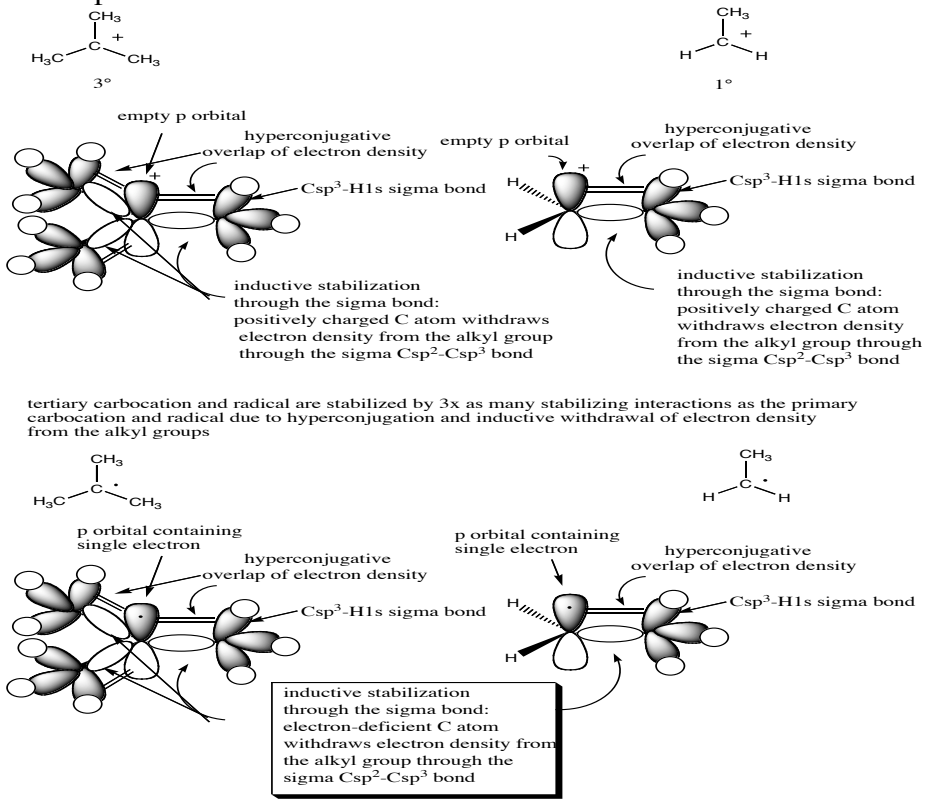
Additional Problems for practice:

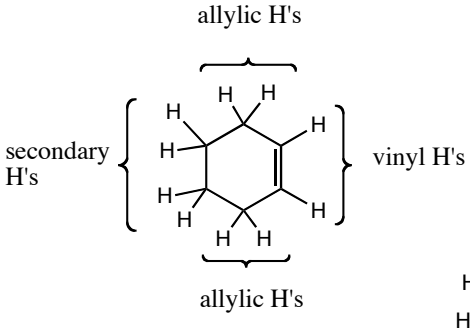
1.) Draw a reaction profile (graph of energy versus reaction coordinate) for a one step reaction with a late transition state. State whether the transition state resembles the starting material or the product. Repeat the process for a one step reaction with an early transition state.



2.) Draw out the structure of a tertiary alkyl carbocation and a primary alkyl carbocation and explain in detail why a tertiary carbocation is more stable than a primary carbocation. Do the same for the corresponding radical species.

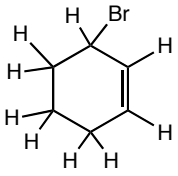


3.) Indicate the preferred site(s) of monobromination (Br_2, hν) for the following molecules. Use bond dissociation energies in table 4-2 in your text as a guide. Remember that bromination is more selective than chlorination.

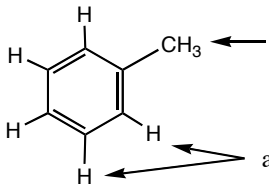


BDE's (table 4-2)

secondary C-H	95 kcal/mol
vinyl C-H	108 kcal/mol
allylic C-H	87 kcal/mol

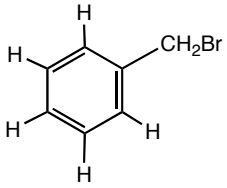


weakest C-H bond: preferred site of bromination

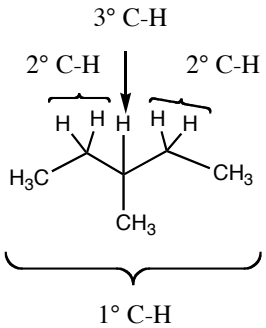


BDE's (table 4-2)

aromatic C-H	110 kcal/mol
benzylic C-H	85 kcal/mol

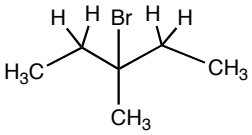


weakest C-H bond: preferred site of bromination



BDE's (table 4-2)

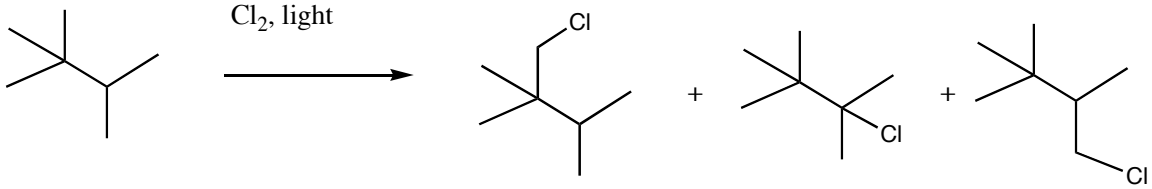
secondary C-H	95 kcal/mol
primary C-H	98 kcal/mol
tertiary C-H	91 kcal/mol



weakest C-H bond: preferred site of bromination

2. Draw the structures of the three possible monochlorination products for the following molecule. Predict the ratios in which these monochlorination products

are formed, remembering that a chlorine atom abstracts a 2° H atom 4.5 x as fast as a 1° H atom, and a 3° H atom is abstracted 5.5 x as fast as a 1° H atom.



44% 27% 29%

type of H	number	relative rate	total	%
primary	9	1	9	9/(9+6+5.5) • 100% = 44%
primary	6	1	6	6/(9+6+5.5) • 100% = 29%
tertiary	1	5.5	5.5	5.5/(9+6+5.5) • 100% = 27%