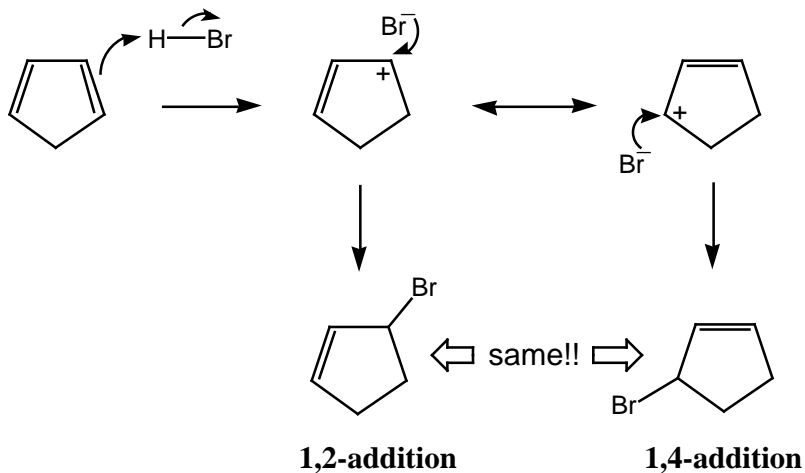
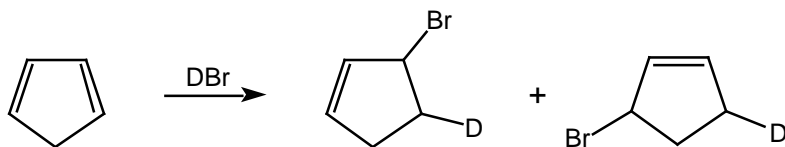


Answers to Problem Set #8
CH241-2001F

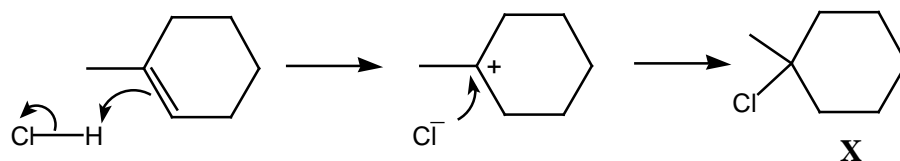
- [1] In this case, the 1,2- and 1,4- addition of HCl lead to the same product.



If we use DBr, instead of HBr, we can tell between the two mechanisms because the products would be different.

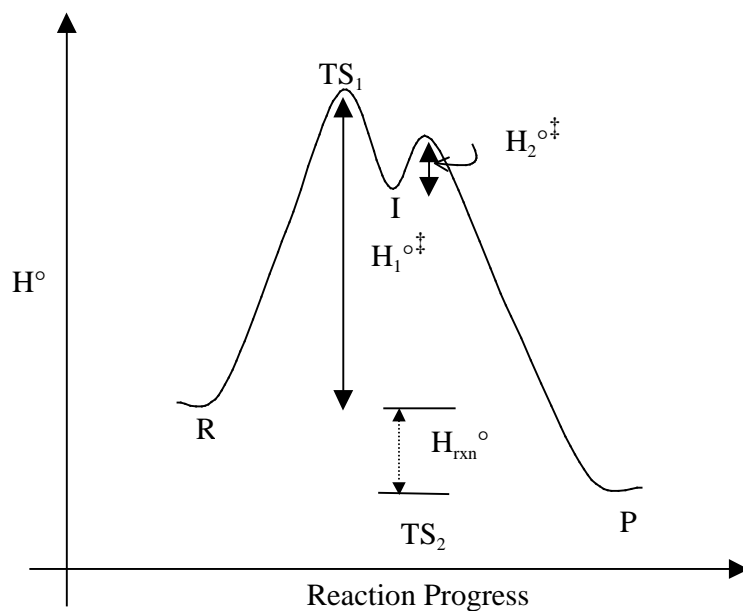


- [2] (a) The tertiary chloride **X** is formed by the usual "Markovnikov" type of addition that involves the more stable tertiary carbocation.

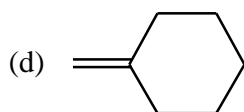


- (b) Bonds broken are worth about 169 kcal/mol (66 for C=C and 103 for H-Cl). Bonds formed are worth about -181 kcal/mol (-96 for a 2° C-H and -85 for C-Cl). So the reaction is exothermic by approximately 12 kcal/mol.

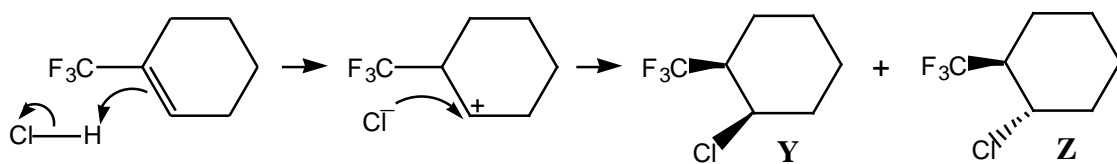
(c) See below. Key to abbreviations are given at the bottom of the diagram.



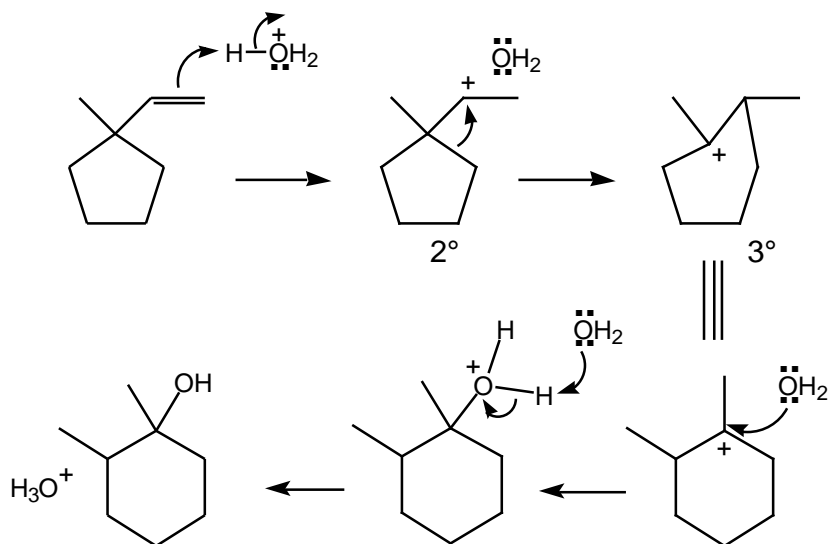
R = 1-methylcyclohexene and HCl; I = carbocation and chloride; P = 1-chloro-1-methylcyclohexane (**X**); The activation barriers for the first and second steps are H_1^{\ddagger} and H_2^{\ddagger} respectively. TS_1 and TS_2 are the transition states for steps 1 and 2 respectively. The difference in enthalpy of product and reactants is H_{rxn}° .



(e) The strongly electron withdrawing CF_3 group would destabilize an adjacent cation. So, in this case, a secondary carbocation is formed.



- [4] (a) The key step here is the rearrangement of the initially formed 2° carbocation to a more stable 3° carbocation.



- (b) Protonation followed by an intramolecular cyclization develops the five-membered ring skeleton. Subsequently, deprotonation occurs from two different sites to give the two products. Please show arrow formalism for the deprotonation step.

