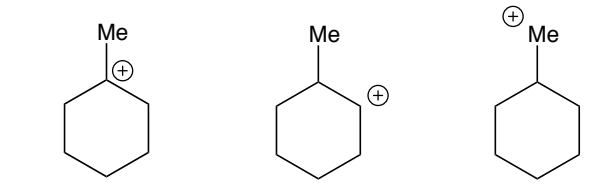
Problem Set 7b

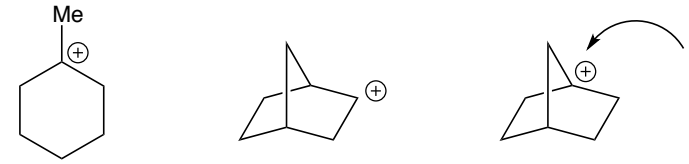
Question 1. Rank the following sets of carbocations from **most to least** stable. *Careful, part (c) is tricky!*

a)



most stable ⟶ least stable

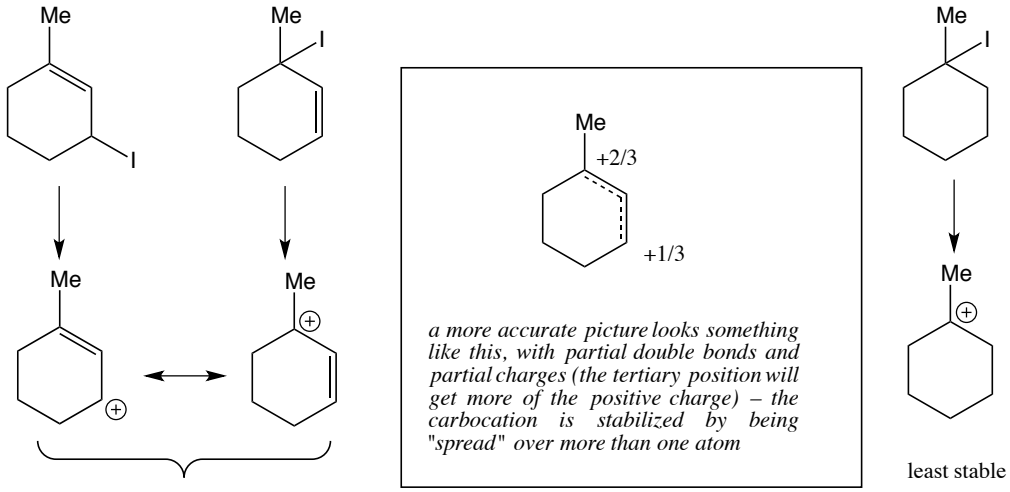
b)



most stable ⟶ least stable

Note: this cation is at a bridgehead. Carbocations are lowest in energy when sp^2-hybridized (planar). This cation, however, cannot be planar (try building a model!). This forces the carbon into sp^3-hybridization, and makes the cation very unstable.

c) The carbocation formed from ionization of the following iodides:



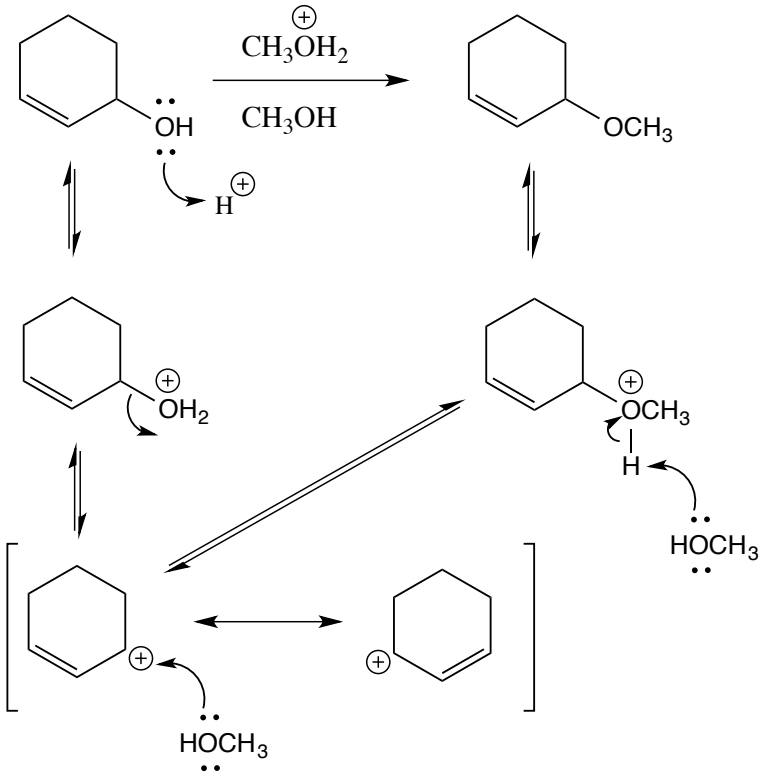
a more accurate picture looks something like this, with partial double bonds and partial charges (the tertiary position will get more of the positive charge) – the carbocation is stabilized by being "spread" over more than one atom

These are resonance structures of the <u>same</u> compound.

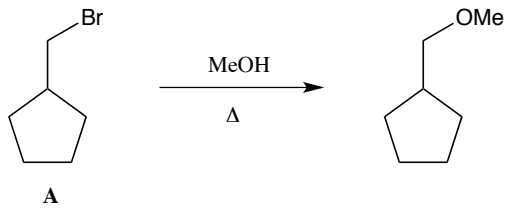
most stable

least stable

Question 2. Provide a complete mechanism (curved arrows showing electron movement) for the following reaction that takes place in acidic methanol. Include all intermediates and resonance structures. *Don't skip any steps!*



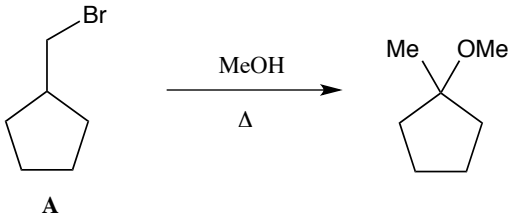
Question 3. a) Explain why heating in primary bromide **A** in methanol does not produce the direct substitution product:



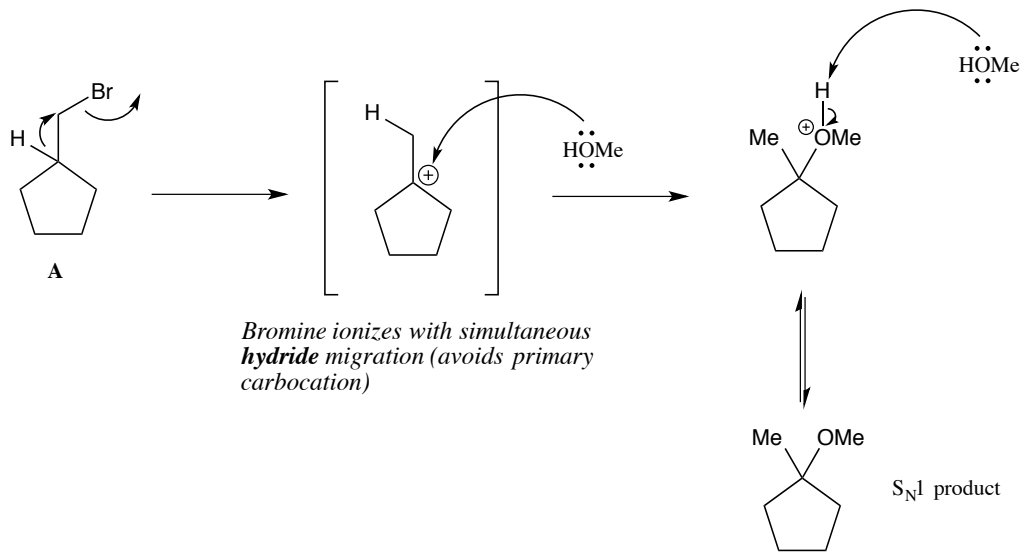
A

Substitution via S_N1 would have to result from a primary carbocation (without migration) – impossible. S_N2 is not favorable with weak nucleophiles.

b) When the reaction above is carried out, a complex mixture of products results. One of the products is the ether shown. Provide a mechanism for the formation of this product.

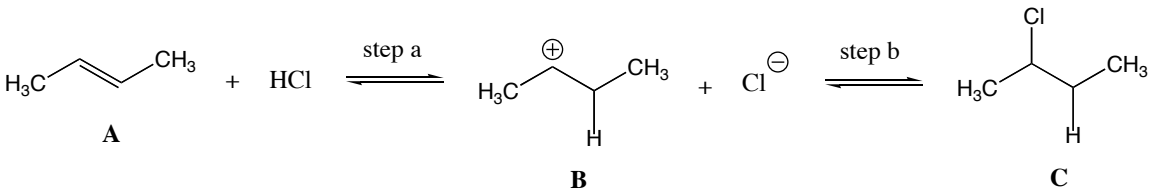


A

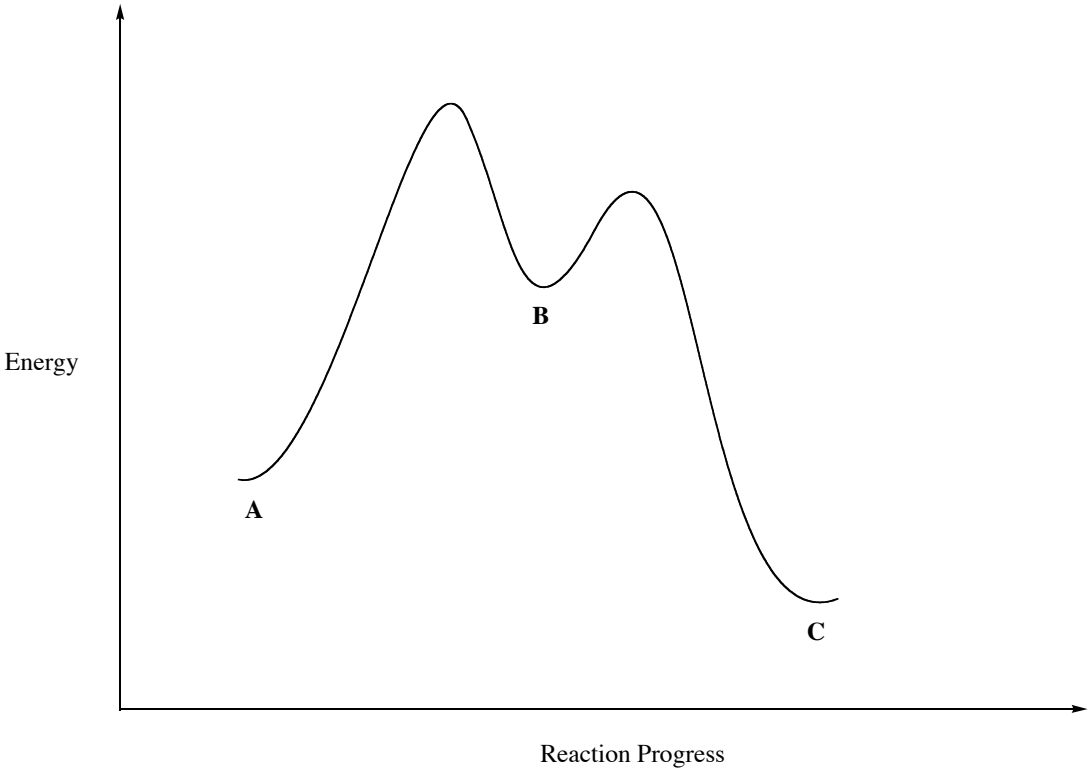


*Bromine ionizes with simultaneous **hydride** migration (avoids primary carbocation)*

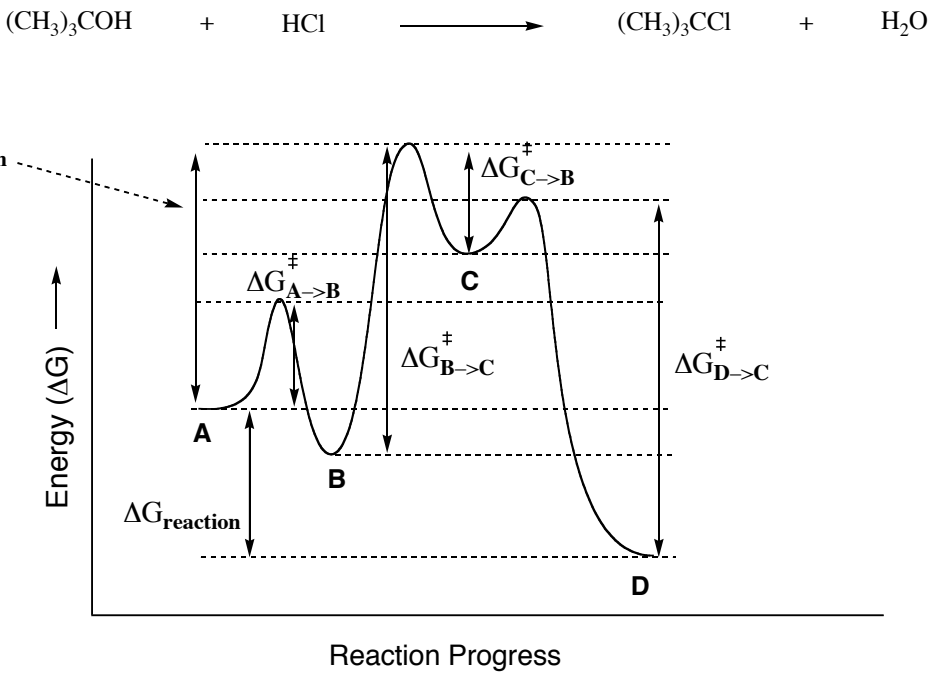
Question 4. Hydrochloric acid can be added across the carbon-carbon double bond of **A** to produce product **C** as detailed below.



Sketch the energy diagram for the reaction above.



Question 5. The following energy diagram depicts the reaction of *tert*-butanol with hydrochloric acid.



a) Is the overall reaction endergonic or exergonic?

Exergonic

b) Match the following four species below with the labels **A–D** on the energy diagram.

D $(CH_3)_3CCl + H_2O$

$(CH_3)_3COH + HCl$ **A**

B $(CH_3)_3\overset{\oplus}{C}OH_2 + Cl^{\ominus}$

$(CH_3)_3\overset{\oplus}{C} + H_2O + Cl^{\ominus}$ **C**

On the energy diagram, label the following:

c) The energy of activation for the reaction
d) ΔG for the overall reaction
e) $\Delta G^{\ddagger}$ for each of the following: **A** –> **B**, **D** –> **C**, **B** –> **C**, and **C** –> **B**