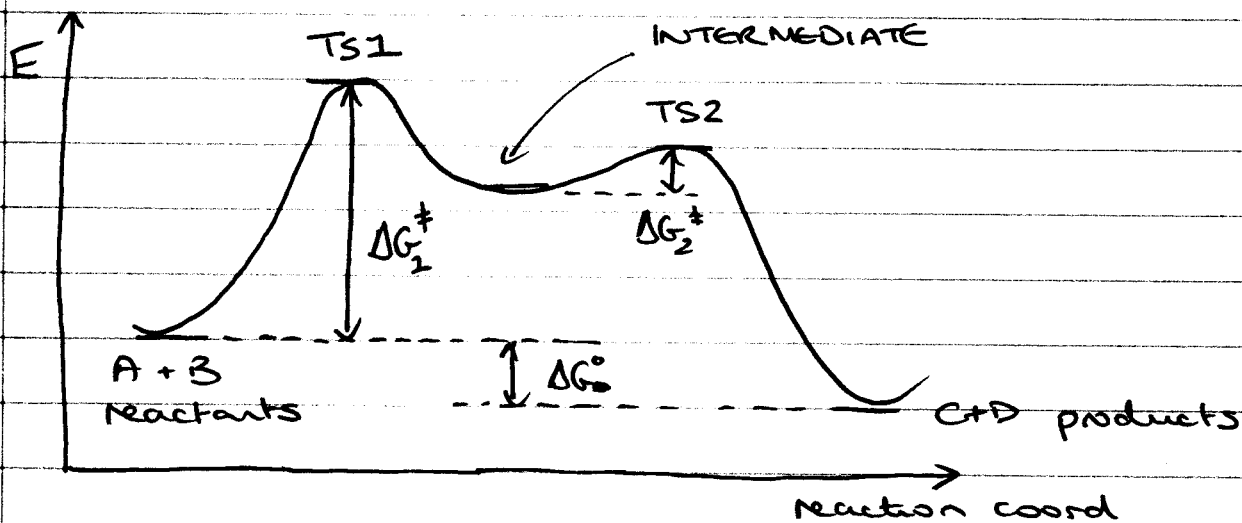


- ① ENERGY PROFILES
 - ② ADDITION TO ALKENES
 - ③ CARBOCATIONS
 - ④ ADDITION OF Br_2/Cl_2
- ← (i) ADDITION OF H_2O
(ii) REARRANGEMENT

HWK: Read 6-6.5 Prob 6.3-6.8, 6.14-6.16
Quiz on WEDNESDAY

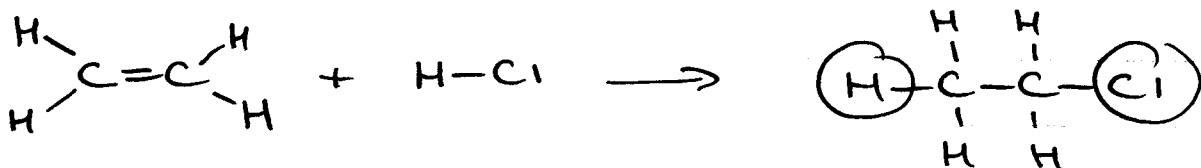
① ENERGY PROFILES



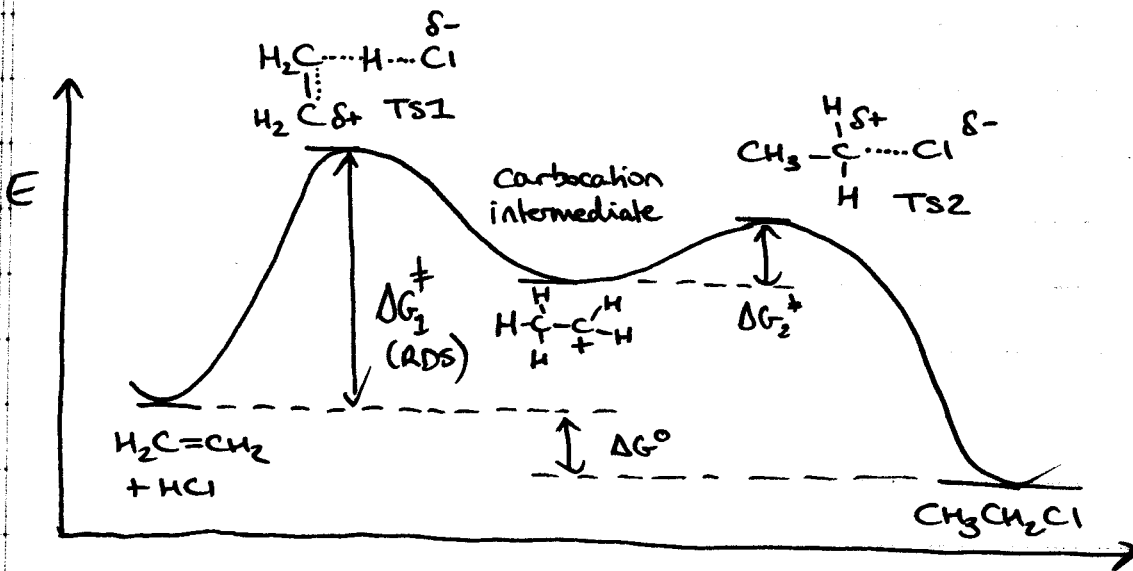
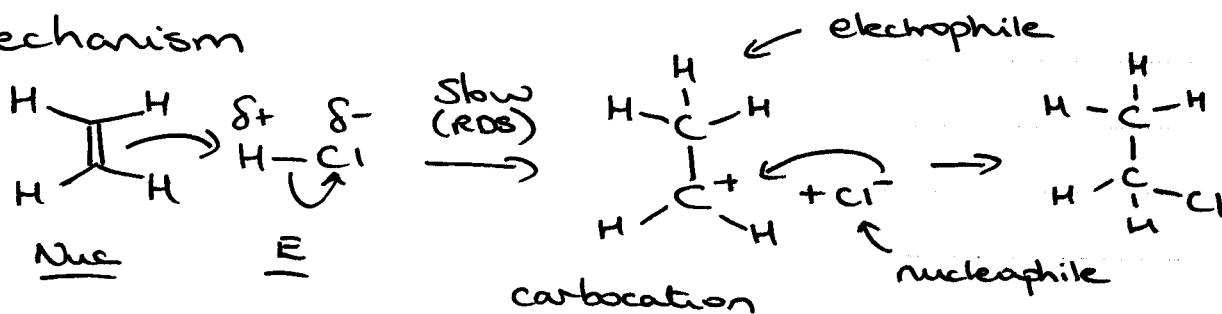
REACTION INTERMEDIATE \Rightarrow localized energy minimum between two TRANSITION states (sometimes possible to isolate)

Slowest step in a multistep process (one w/ highest barrier) is called the RATE DETERMINING STEP (RDS)

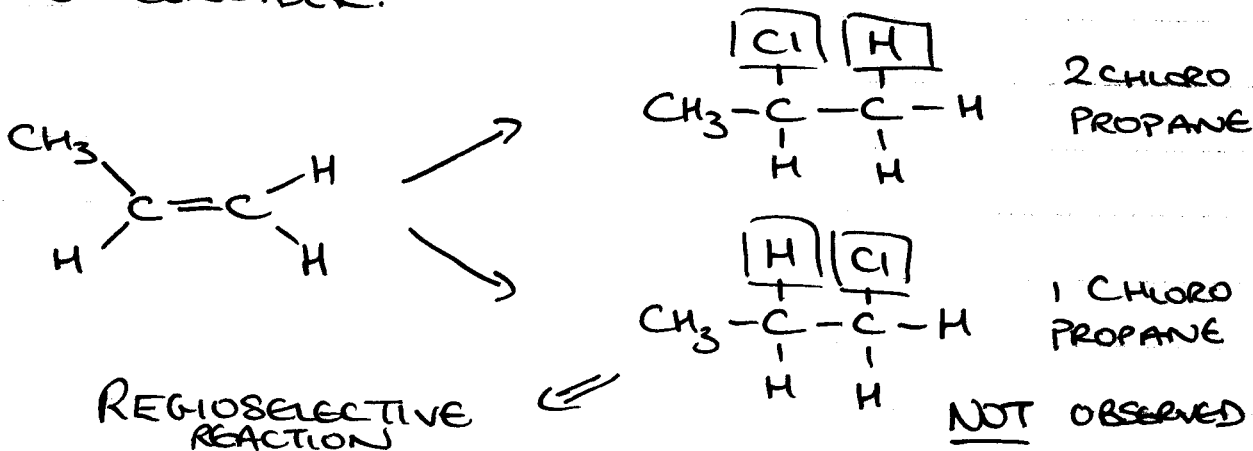
② ELECTROPHILIC ADDITION TO ALKENES



mechanism



NOW CONSIDER:

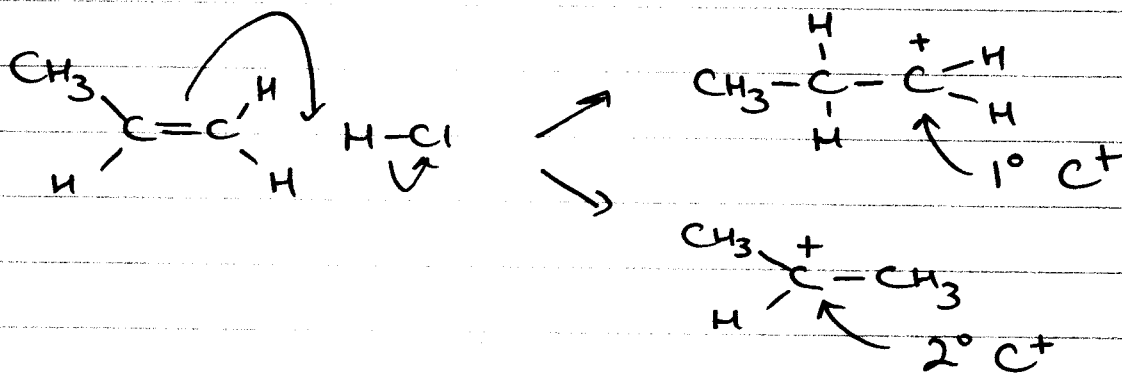


3

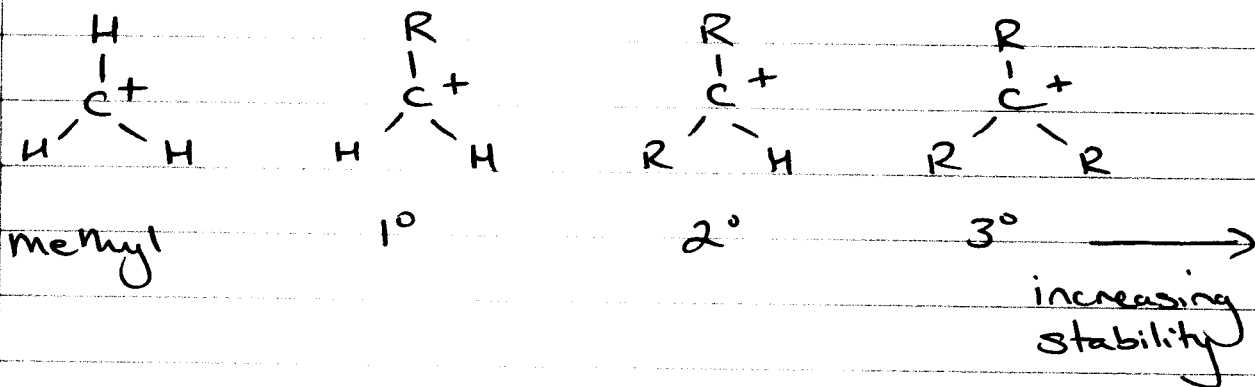
MARKOVNIKOV'S RULE:

Addition of H-X to an ALKENE, H adds to the double bonded C atom with greatest number of H atoms.

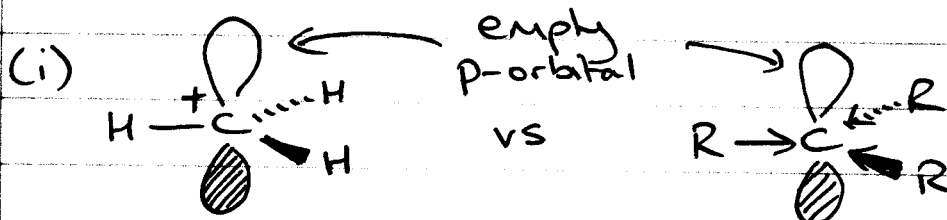
WHY? \Rightarrow CARBOCATIONS (3)



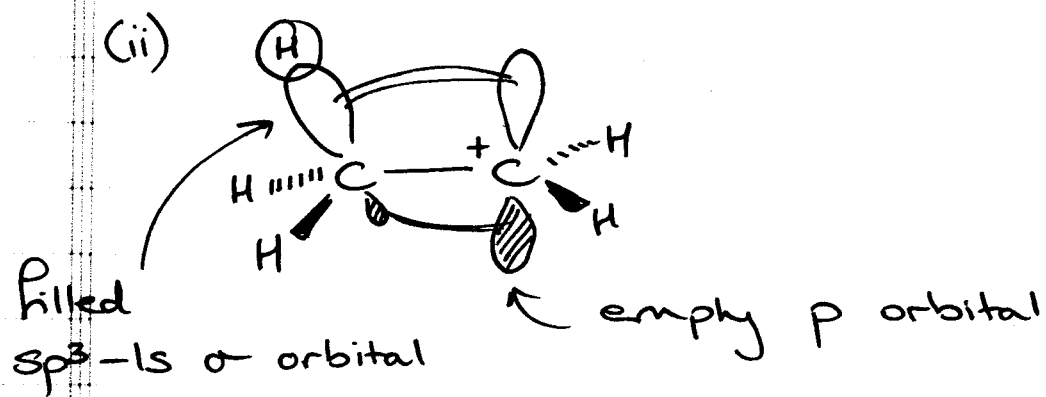
STABILITY (R = ALKYL)



TWO FACTORS: (i) INDUCTIVE EFFECT (ii) HYPERCONJUGATION



ALKYL GROUPS ARE INDUCTIVELY DONATING



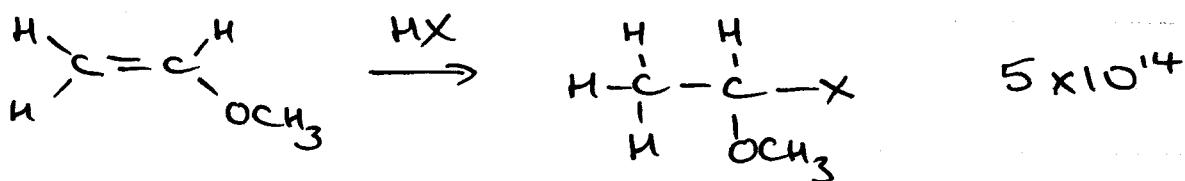
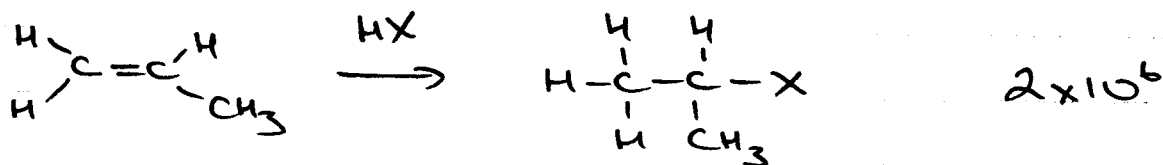
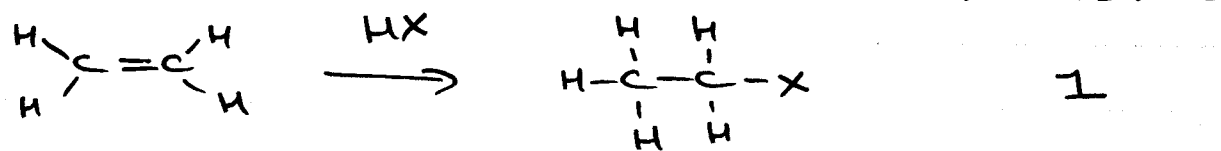
Delocalization of an adjacent σ bond's electrons into the empty p-orbital

\Rightarrow HYPERCONJUGATION

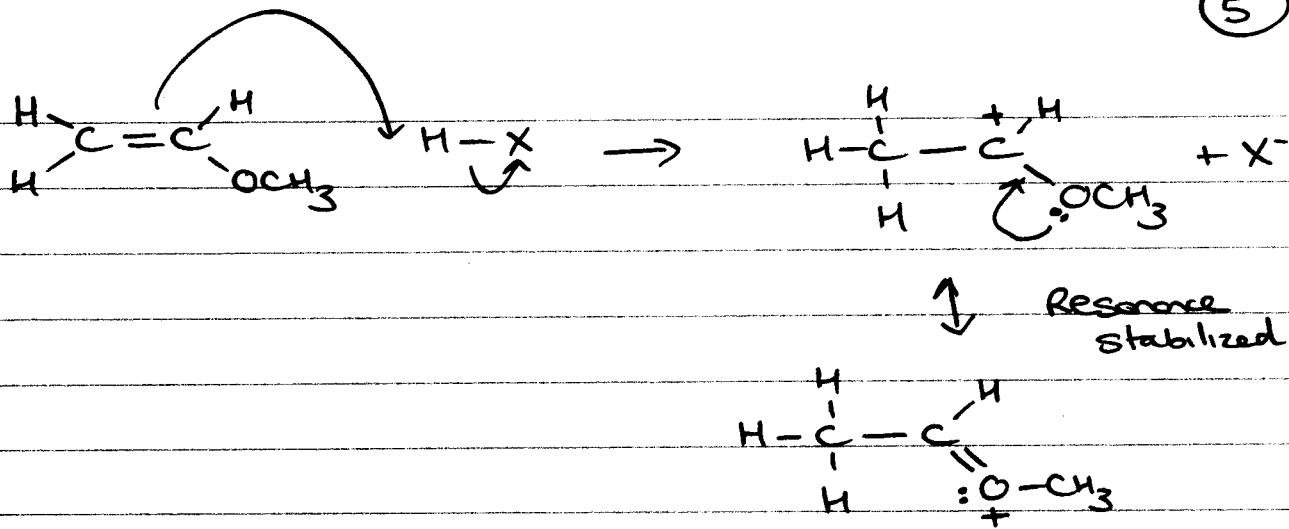
The more C-H bonds, the more significant the stabilization, so $Met < 1^\circ < 2^\circ < 3^\circ$

.... AND OTHER FACTORS.... (RESONANCE)

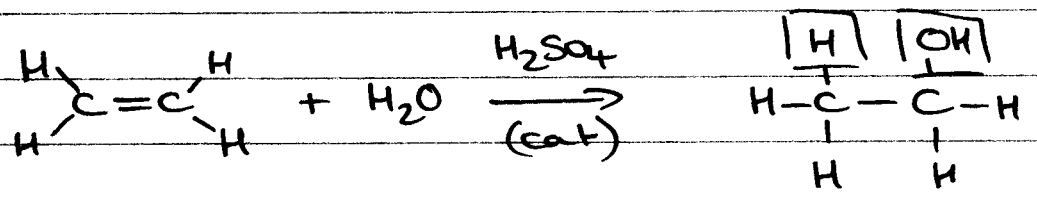
consider:



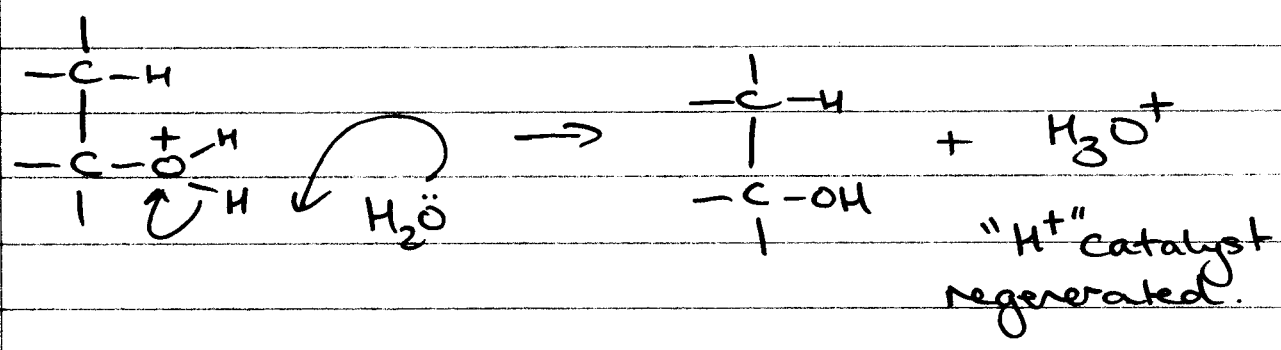
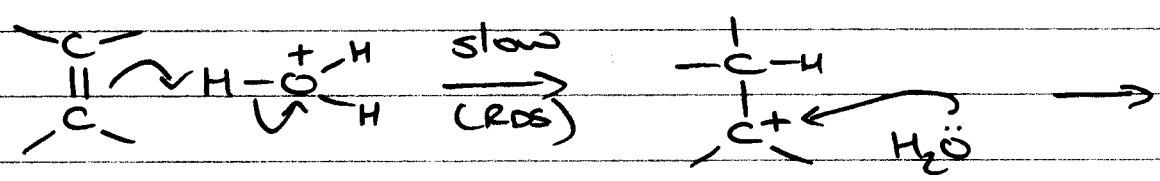
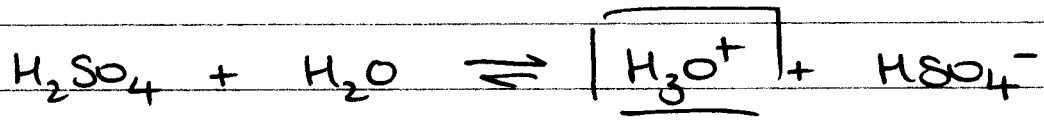
(5)



(i) ~~ii~~ ADDITION of H₂O (acid catalyzed hydration)

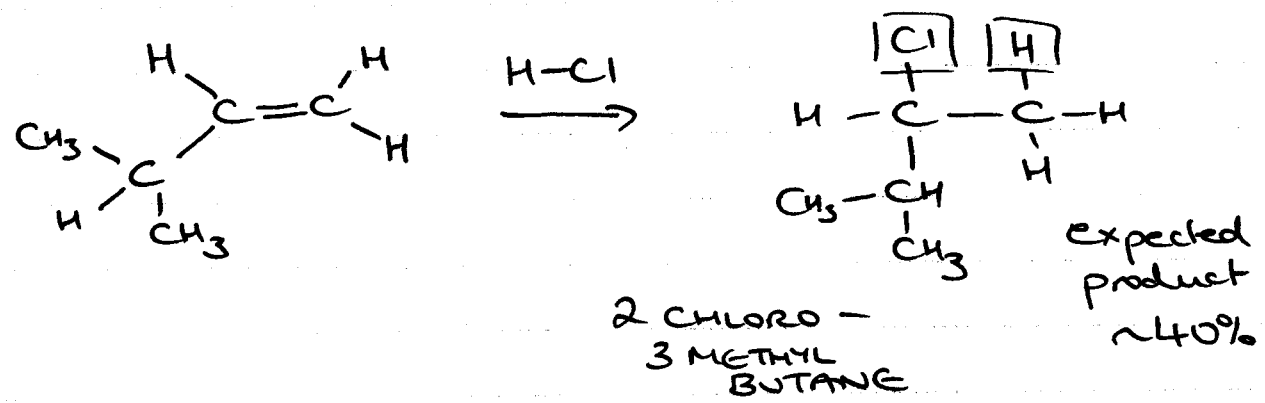


H₂O cannot protonate a C=C bond, like H-Cl or H-Br, but:

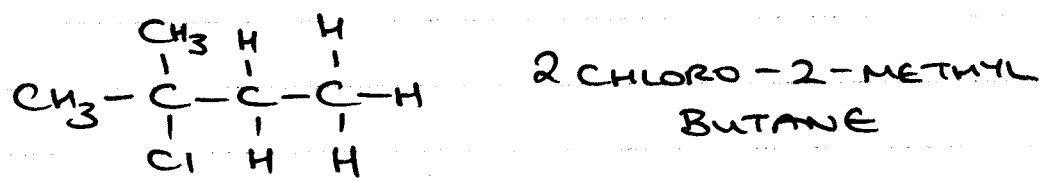


mechanism involves a carbocation, so proceeds with MARKOVNIKOV regioselectivity

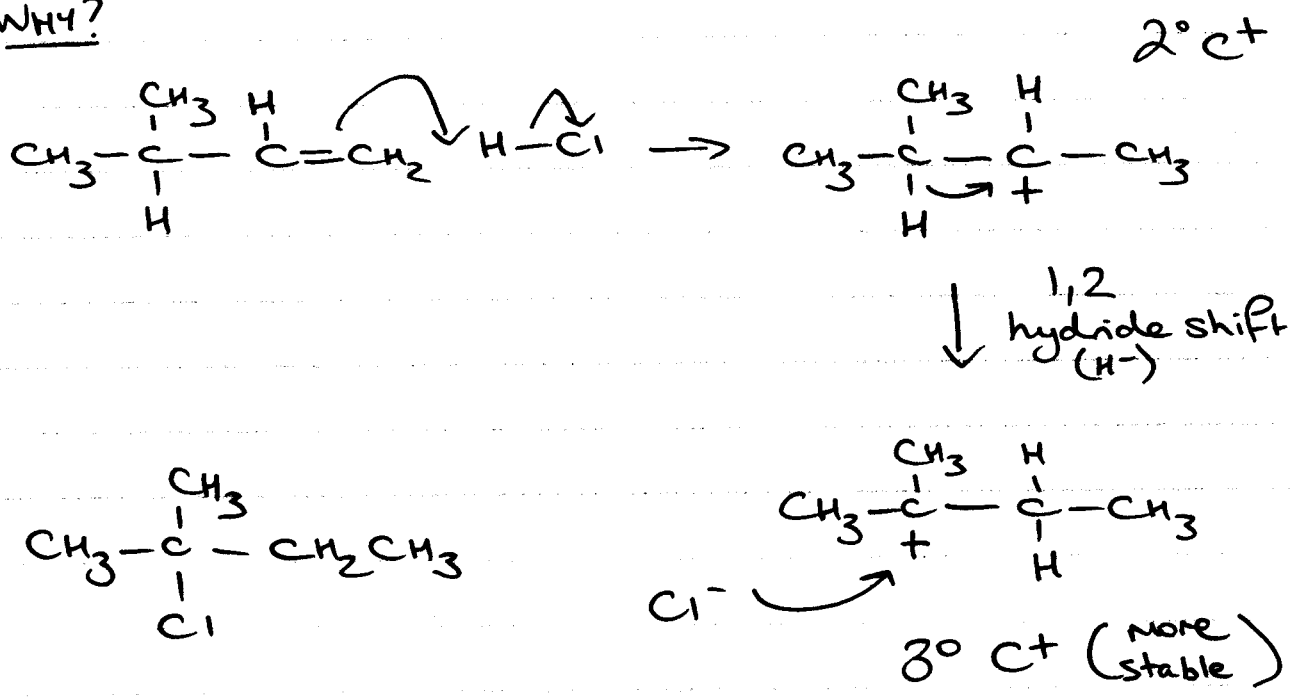
(ii) - CARBOCATION REARRANGEMENT



- other 60% ?

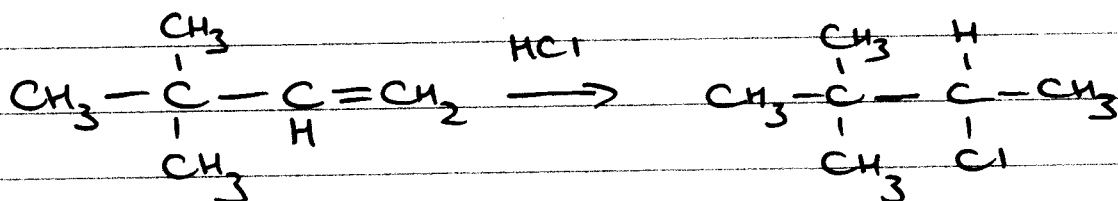


WHY?



(7)

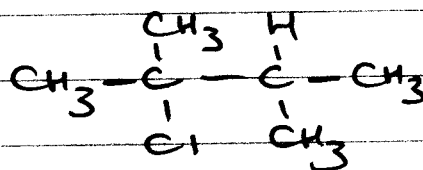
Rearrangement can happen whenever you have a CARBOCATION, so also happens in ACID cat hydration



Minor (20%)

SHOW WHY THIS HAPPENS \Rightarrow

(NOT A H⁻ SHIFT, BUT A 1,2 METHYL SHIFT)



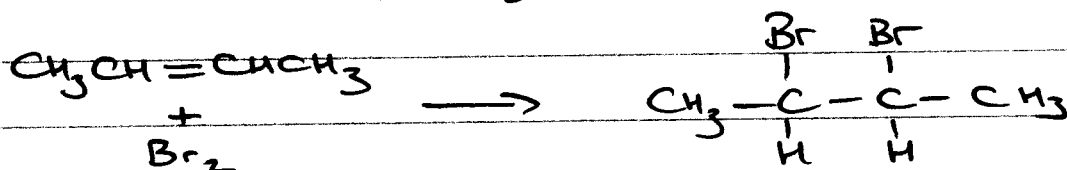
Major (80%)

2° CARBOCATIONS \rightleftharpoons 3° CARBOCATIONS

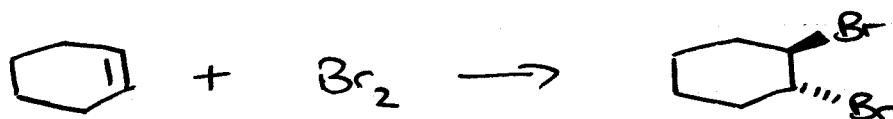
(v. rarely rearrange in reverse direction)

Don't really need to worry about 1° C⁺ as in reality they do not form during reactions in solution as they are so unstable.

(4) ADDITION of Br₂/Cl₂



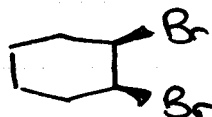
Note



trans 1,2-dibromo
cyclohexane

STEREOSPECIFIC REACTION

DO NOT FORM ANY



— WHY?