LEC (14) CHEM 30A Nov 3rd

1. KINETICS vs THERMODYNAMICS
2. ADDITION TO ALKENES
   - HX
   - H_2O
3. CARBOCATION REARRANGEMENT
4. ADDITION OF Br_2 / Cl_2

HMK: Read 6-6.5
Problems 6.3 - 6.8, 6.14 - 6.16

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1. KINETICS vs THERMODYNAMICS

↓	↓
How fast will it happen	will a reaction happen

e.g.

$$+ \; O_2 \rightleftharpoons 8CO_2 + 9H_2O$$

isooctane $\Delta G^\circ = -1000\ kJ\ mol^{-1}$

$K_{eq} = 10^{175}$ at 298K

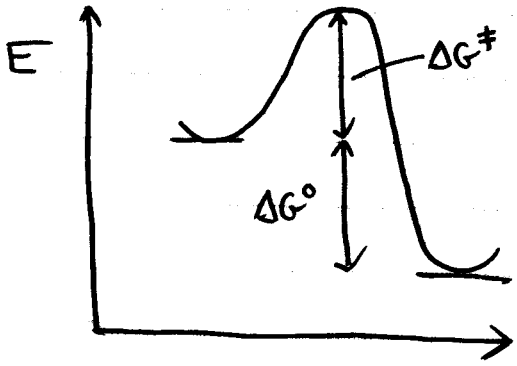
(10^{86} atoms in the observable universe)

BUT

Isooctane is stable
(you put it in your car...)

Energy is required to start the reaction
⇒ ACTIVATION ENERGY

→ spark plug



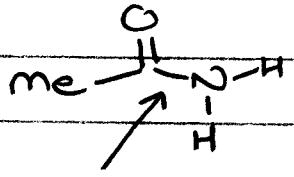
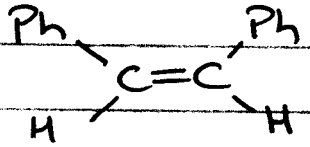
So isooctane + oxygen

THERMODYNAMICALLY UNSTABLE
BUT KINETICALLY STABLE

However → apply burst of energy to $H_2O + CO_2$, they will not reconvert to octane and oxygen.

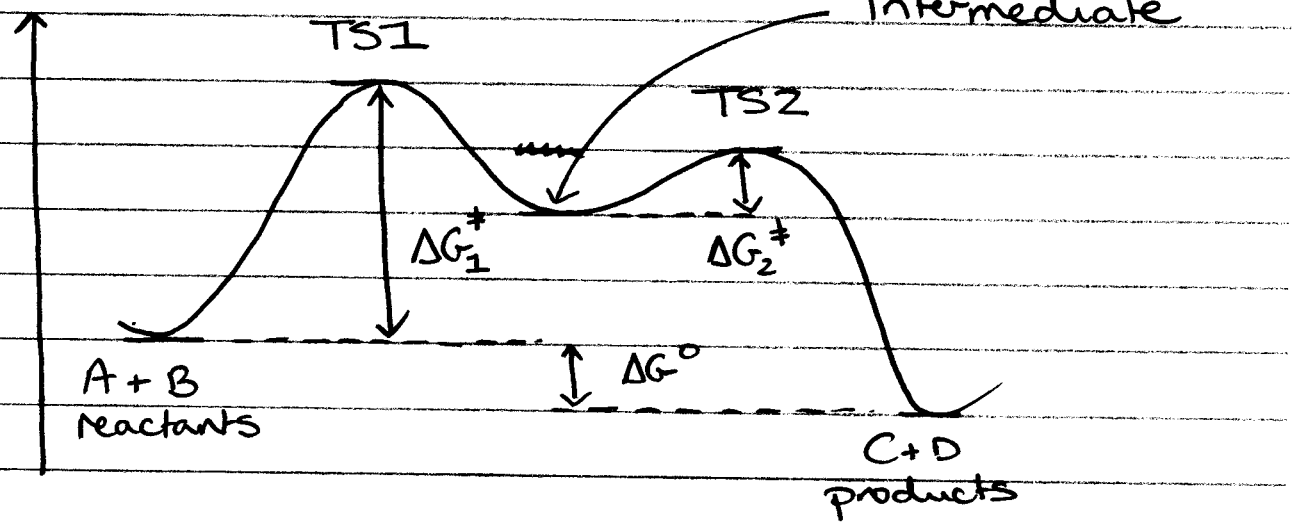
ENERGY BARRIERS & RATE

(Consider BOND ROTATION - same principles apply to reactions)

	E_A (kcal/mol)	k (s^{-1}) (298 K)	$t_{1/2}$
H_3C-CH_3	3	5×10^{10}	0.02 ns
Cl_3C-CCl_3	11	8×10^{4}	10 μs
	17	3	0.2 s
	45	2×10^{-19}	~ 10^{11} years

(AGE of the EARTH ~ 4.6×10^9 years)

- TWO-STEP REACTION

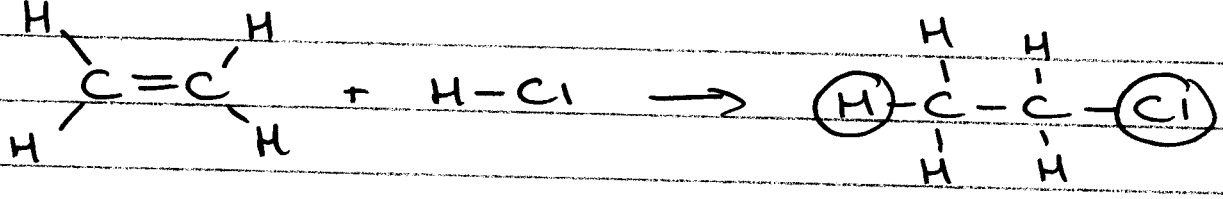


Reaction Intermediate
=> localized energy minimum between two transition states

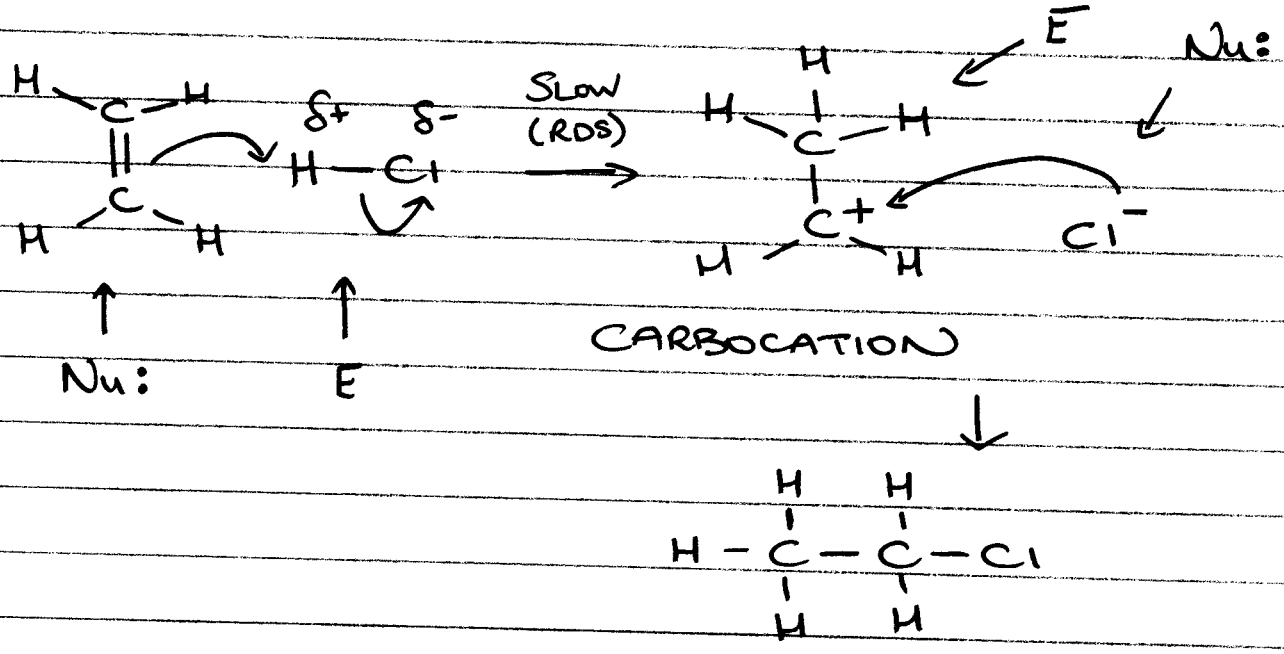
(sometimes possible to isolate)

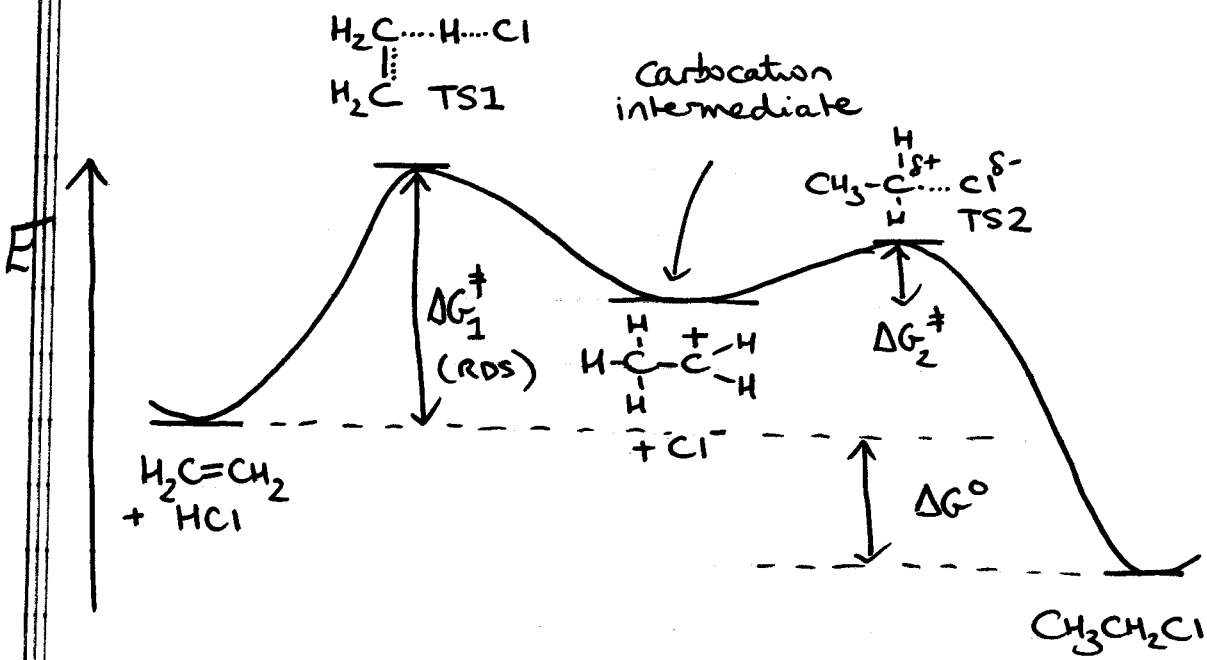
Slowest step in a MULTISTEP reaction (one with highest barrier) is called the rate determining step (RDS)

(2) ELECTROPHILIC ADDITION TO ALKENES

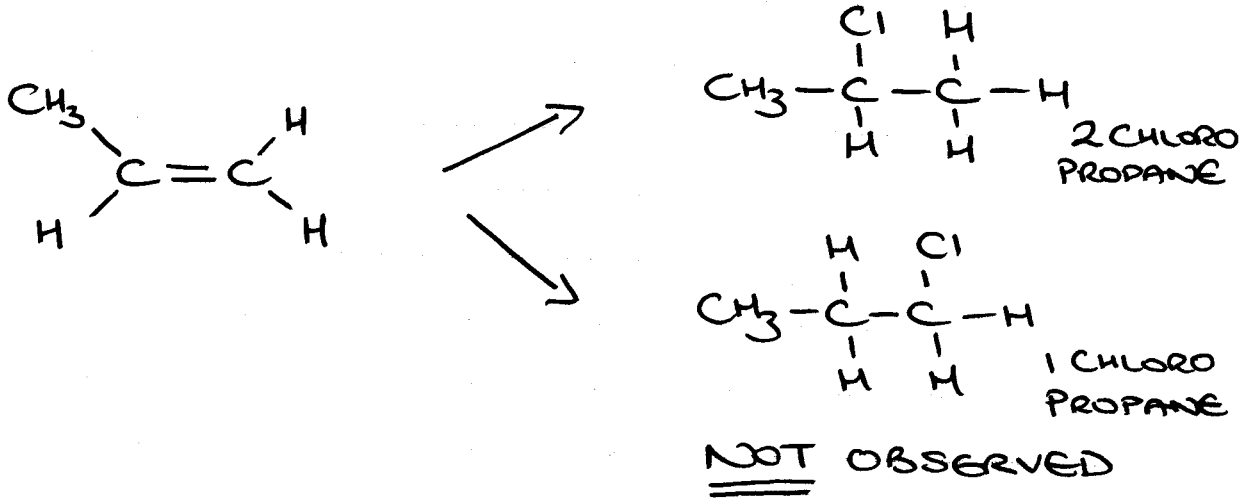


Mechanism





NOW CONSIDER:



NOT OBSERVED

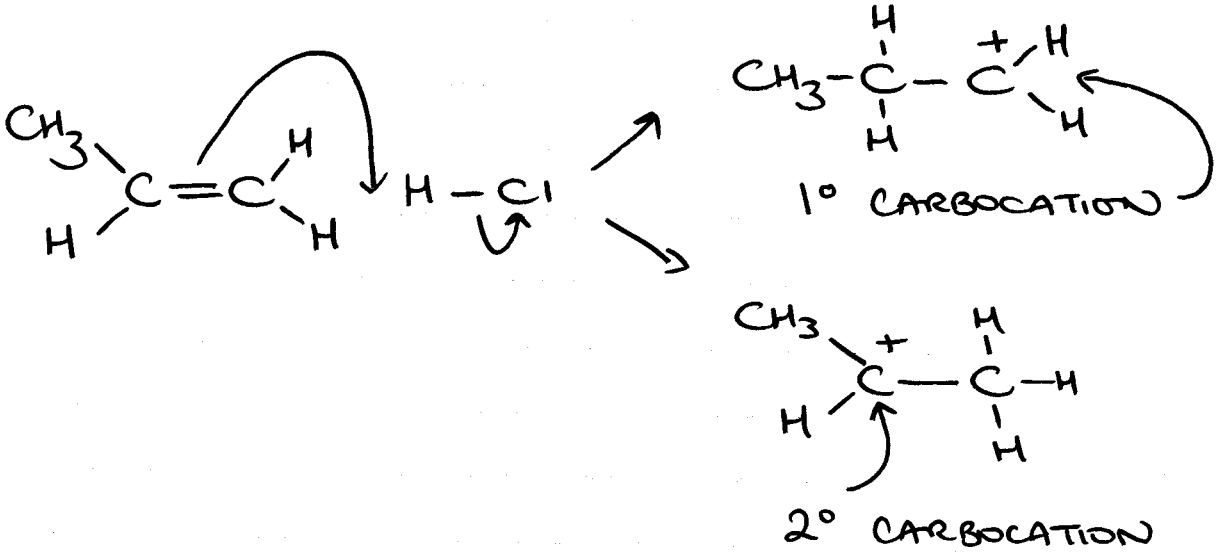
Example of a REGIOSELECTIVE reaction

MARKOVNIKOV'S RULE —

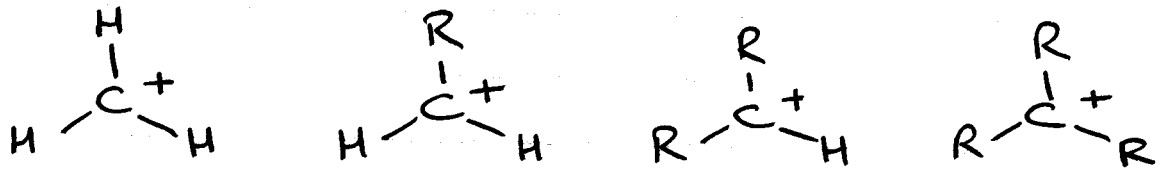
Addition of H–X to an ALKENE, H adds to double-bonded C atom with greatest # of H atoms

WHY?

CARBOCATIONS



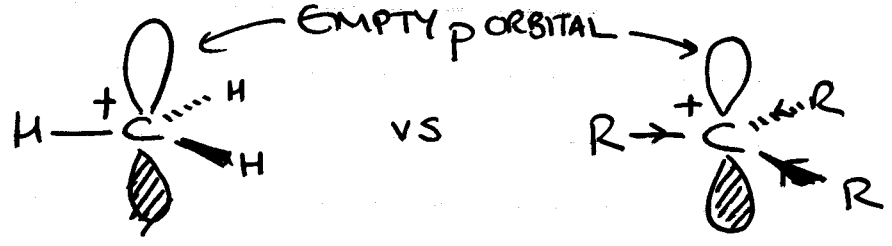
STABILITY (R = ALKYL)



INCREASING STABILITY →

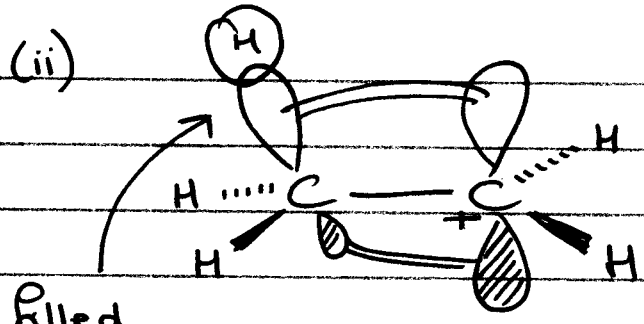
TWO FACTORS: (i) INDUCTIVE EFFECT
(ii) HYPERCONJUGATION

(i)



ALKYL GROUPS ARE INDUCTIVELY DONATING

(ii)



filled sp^3–1s σ orbital

↖ empty p orbital

DELOCALIZATION of adjacent σ BOND e^- into the empty p-orbital

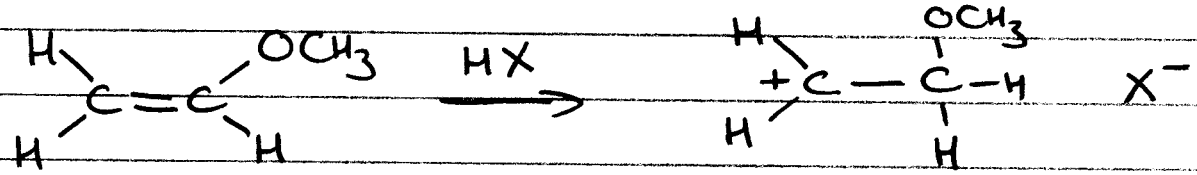
– HYPERCONJUGATION

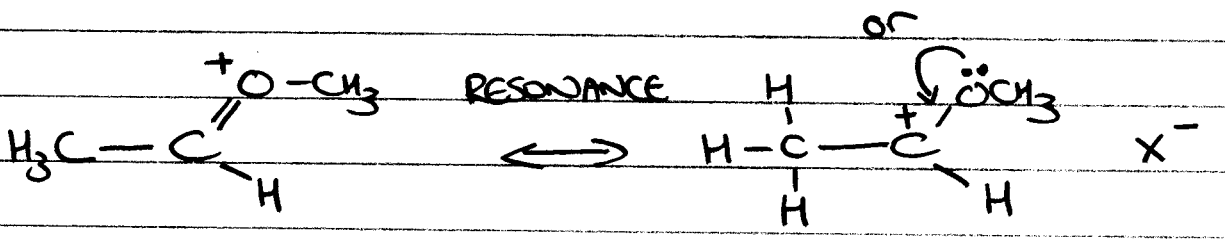
– the more C–H bonds, the more significant the interaction, so

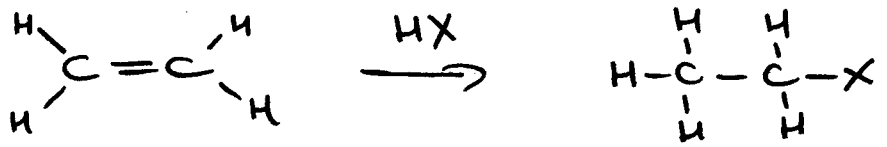
$Me^+ < 1° < 2° < 3°$

.... AND ANOTHER FACTOR → RESONANCE

consider

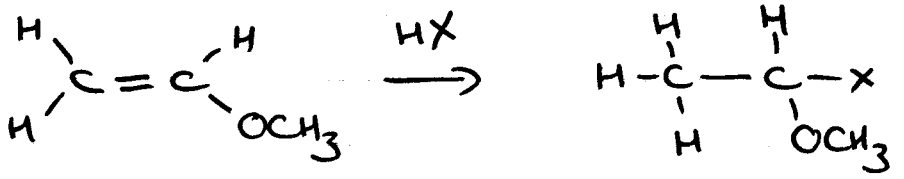






1

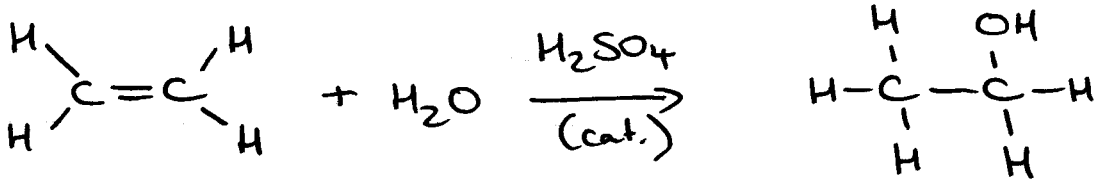
2×10^6



5×10^{14}

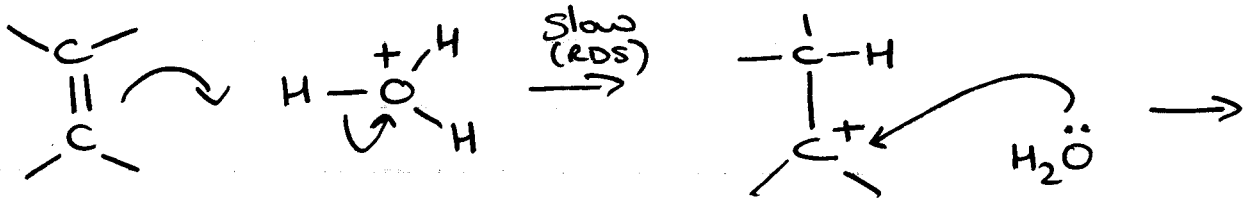
RELATIVE RATES of ADDITION at 298K

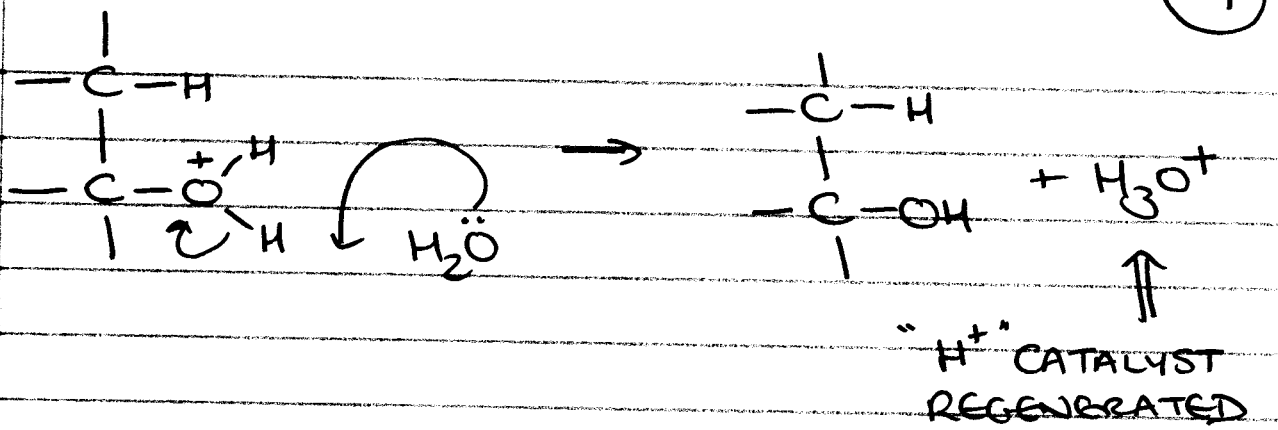
ADDITION OF H_2O (acid catalyst)
(HYDRATION)



H_2O cannot protonate a C=C bond like HCl or HBr, but

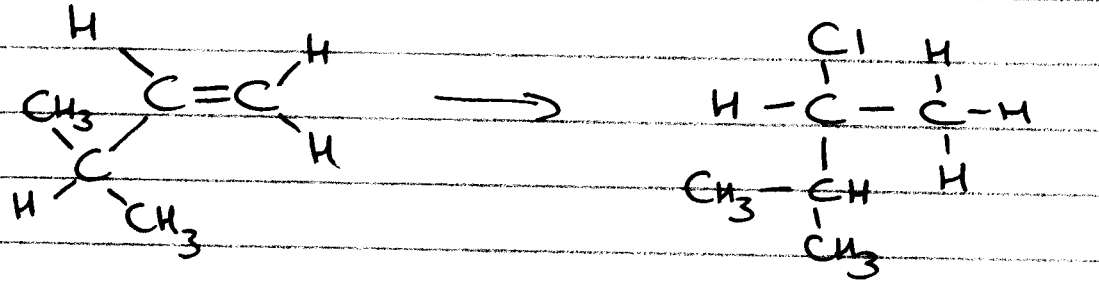
$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$





Mechanism involves a carbocation, so proceeds with MARKOVNIKOV selectivity.

③ CARBOCATION REARRANGEMENT

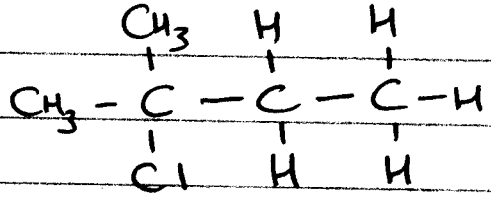


Expected product

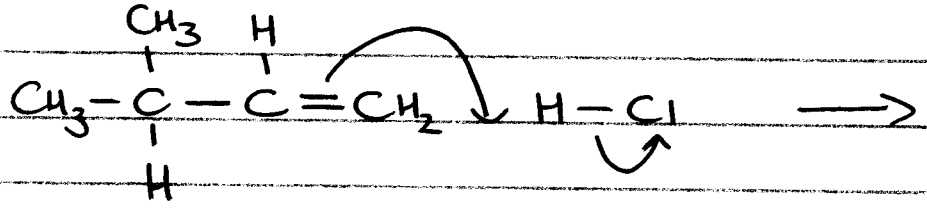
~ 40%

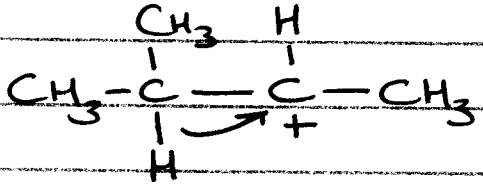
2CHLORO-3-METHYL BUTANE

other 60% ?

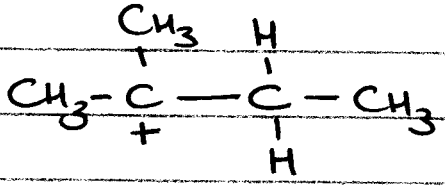


2 CHLORO-2-METHYL BUTANE





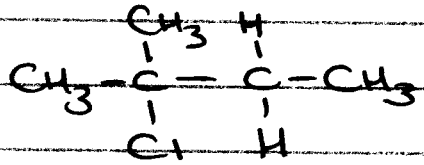
1,2 HYDRIDE SHIFT



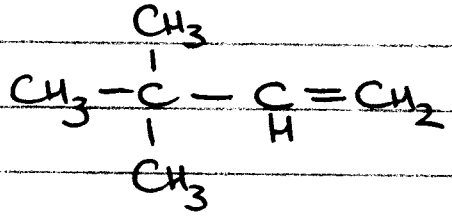
Secondary carbocation

tertiary carbocation (more stable)

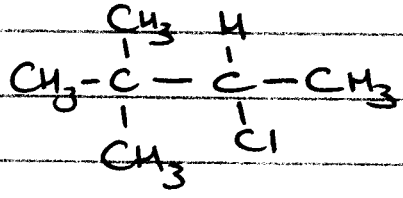
Cl^-



Can also happen in ACID CATALYSED HYDRATION

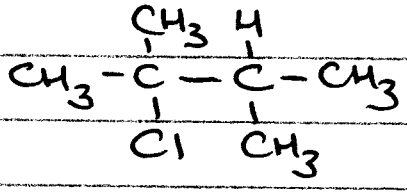


HCl



MINOR PRODUCT (20%)

INVOLVES A 1,2 METHYL SHIFT



MAJOR PRODUCT (80%)

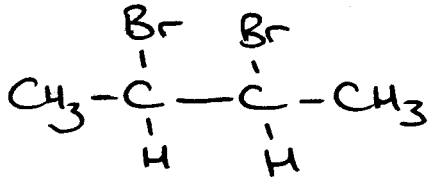
SHOW WHY THIS HAPPENS

2° CARBOCATIONS → 3° CARBOCATIONS

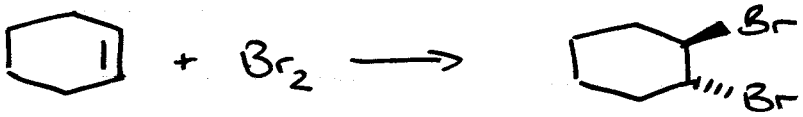
(RARELY REARRANGE IN THE OPPOSITE DIRECTION)

We don't really worry about 1° C+, as they don't form in reactions in solution as they are UNSTABLE.

(4) ADDITION of Br_2 / Cl_2

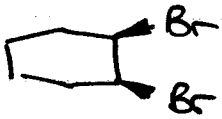
$CH_3CH=CHCH_3 + Br_2 \longrightarrow$ 

note:



trans
1,2-dibromocyclohexane

AN EXAMPLE OF A STEREOSPECIFIC REACTION

– DO NOT FORM  – WHY?