

LEC (25)

CHEM 30A

Dec 6m

(1)

- | | |
|------------------------|-----------|
| ① RADICAL MECHANISMS | WEDS |
| ② HAMMOND POSTULATE | - QUIZ |
| ③ RADICAL STRUCTURE | - EVALS |
| ④ RADICAL STABILITY | |
| ⑤ ALLYLIC HALOGENATION | FRIDAY |
| | - WRAP UP |

READ - CH 7

PROBLEMS: 7.4, 7.5 - 7.27

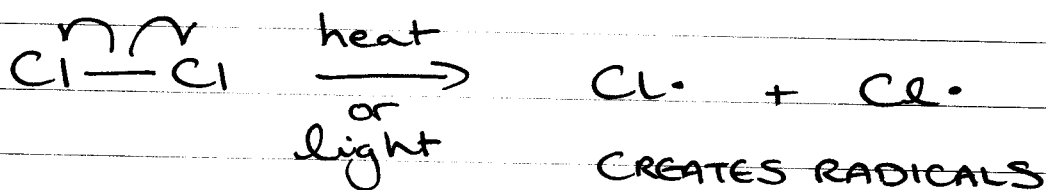
FRIDAY 17th
FINAL

① RADICAL MECHANISMS

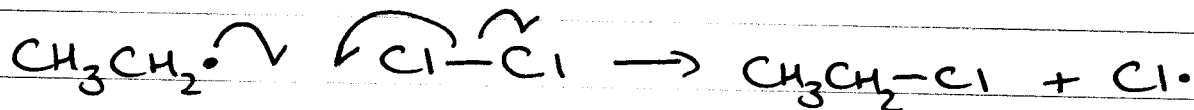
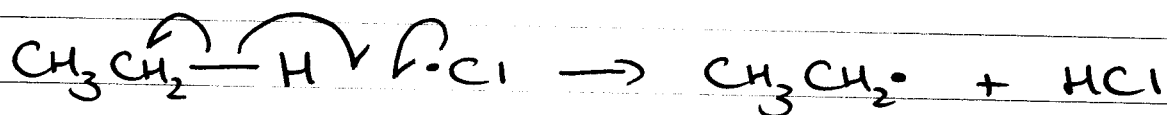
THREE STEPS INITIATION / PROPAGATION / TERMINATION



(i) CHAIN INITIATION

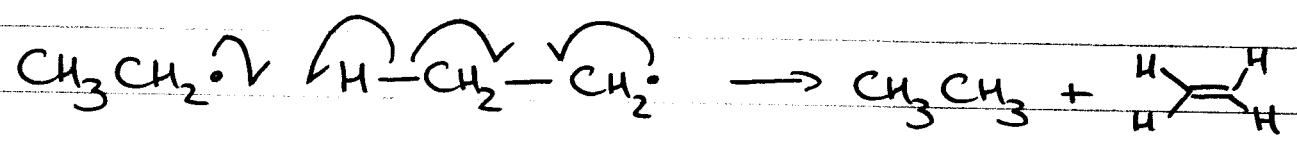
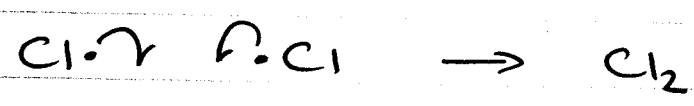
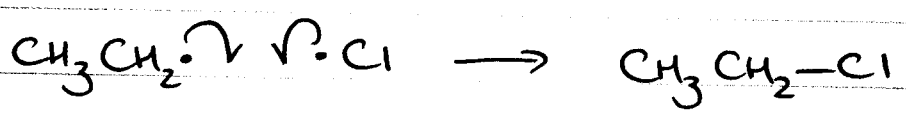
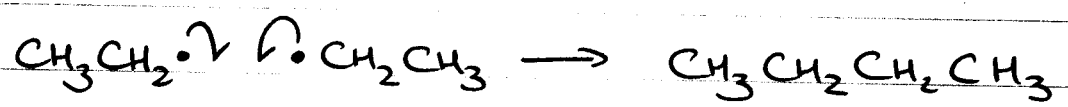


(ii) CHAIN PROPAGATION



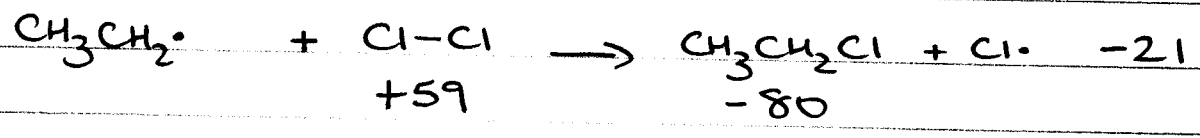
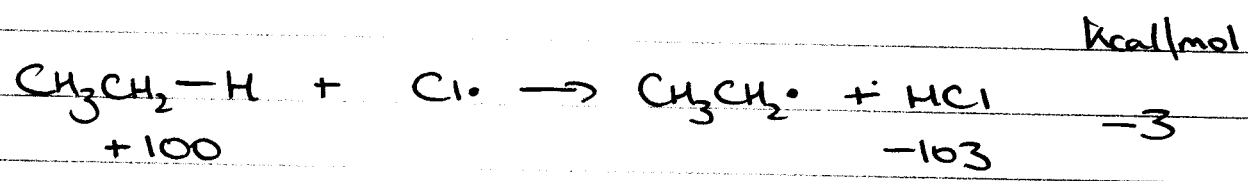
PROPAGATES RADICALS

(iii) CHAIN TERMINATION

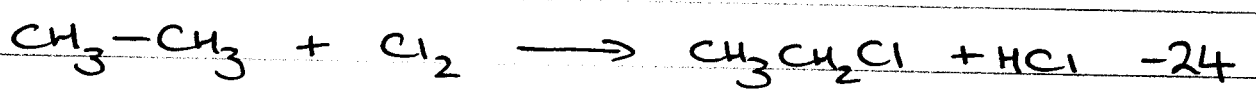


CONSUMES RADICALS

CHAIN PROPAGATION can happen many times before termination → number of cycles is called the CHAIN LENGTH



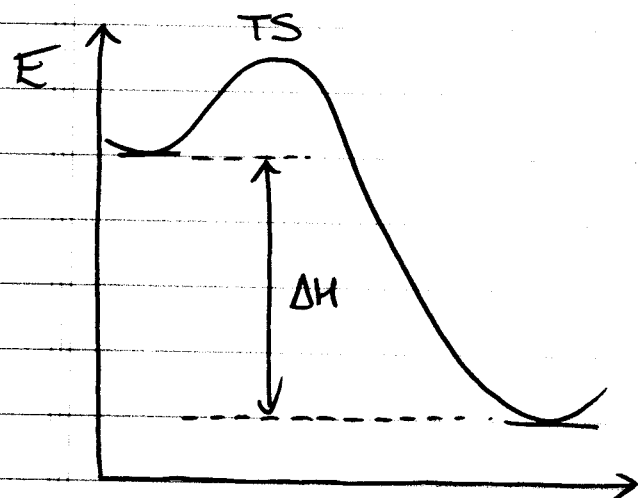
ADD TOGETHER



Gives reaction stoichiometry and heat of reaction (ΔH)

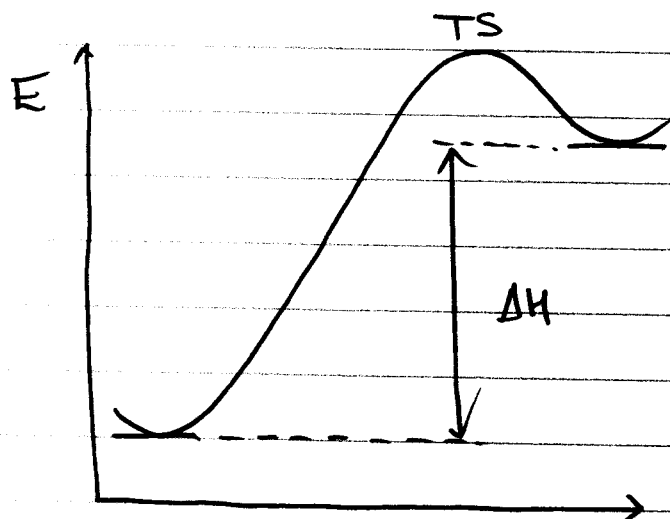
② HAMMOND POSTULATE

- A transition state will be most like the reactant, the intermediate, or the product, if it is close in energy to one of these structures



strongly exothermic reaction

TS looks like reactant

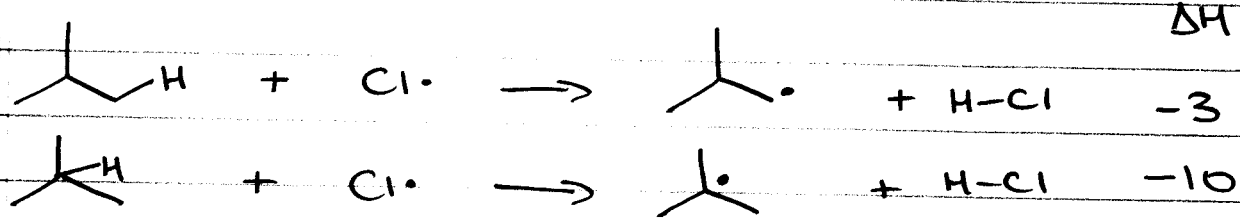


strongly endothermic reaction

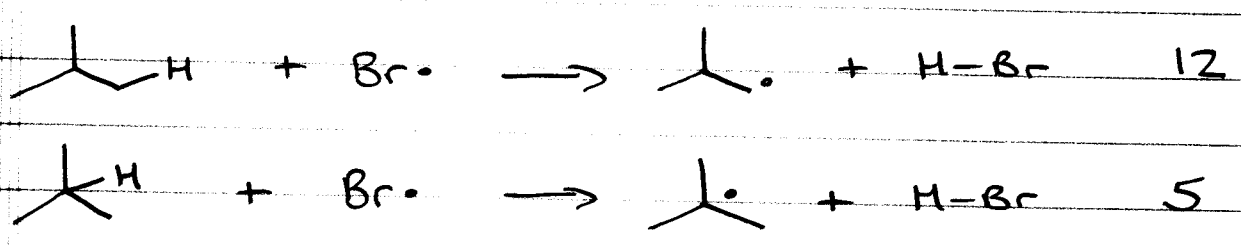
TS looks like product

Consider: (ABSTRACTION of H is RDS)

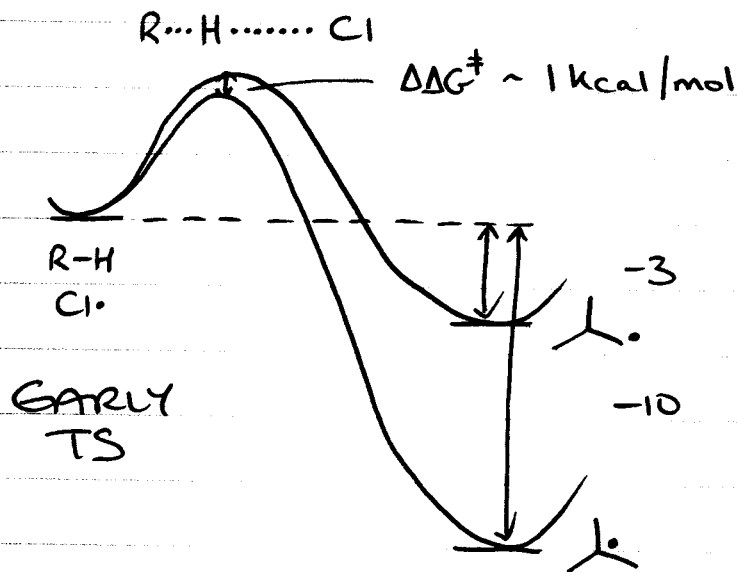
CHLORINATION



BROMINATION

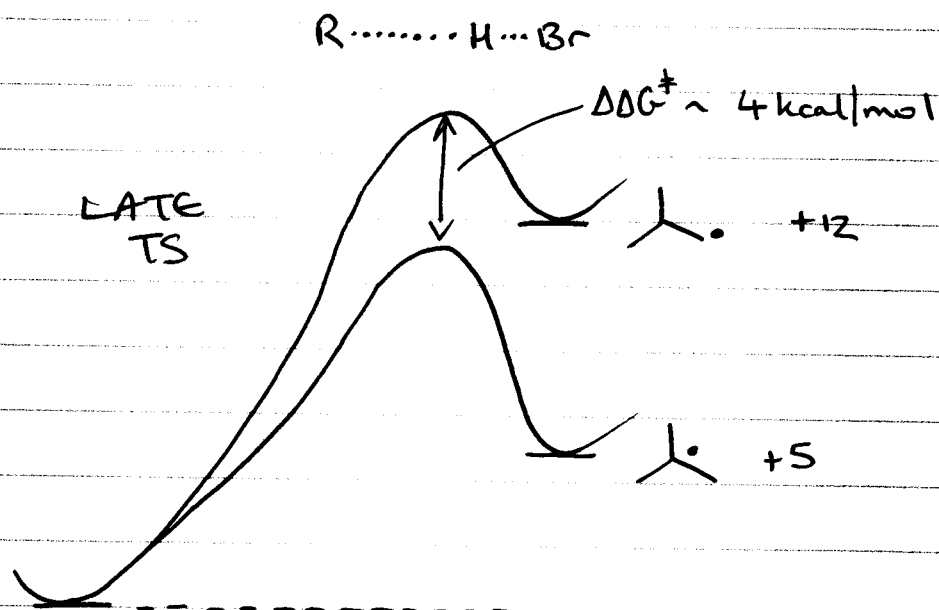


- CHLORINATION (exothermic)



VERY LITTLE
ALKYL
RADICAL
CHARACTER
IN TS

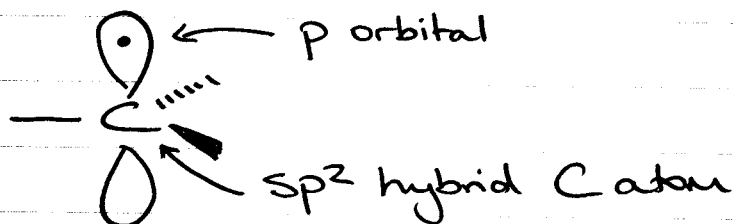
- BROMINATION (endothermic)



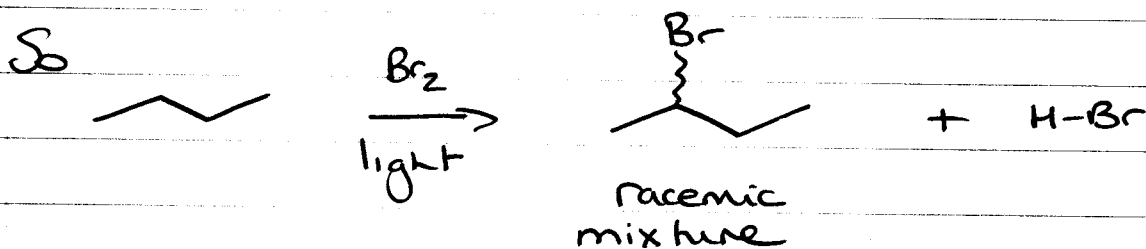
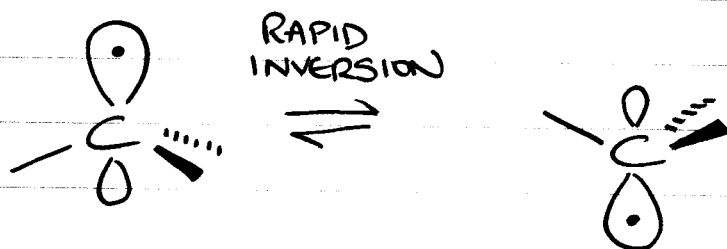
A LOT OF
ALKYL
RADICAL
CHARACTER
IN TS

In BROMINATION, stability of radical is reflected more so in the TS than in CHLORINATION, explaining the MUCH GREATER REGIOSELECTIVITY for radical BROMINATION

③ RADICAL STRUCTURE

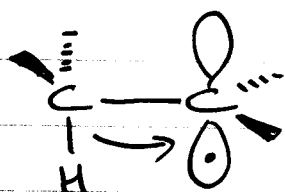
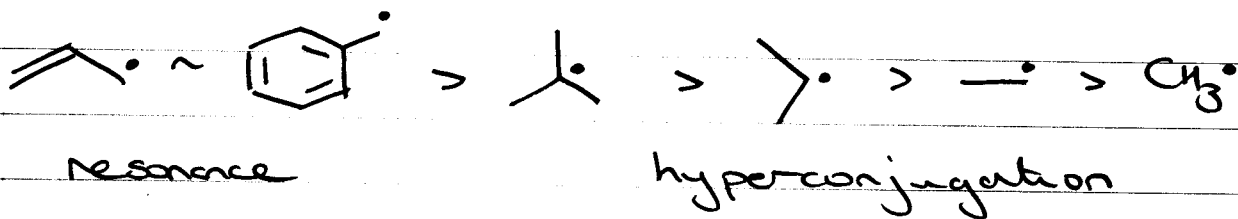


actually shallow pyramid



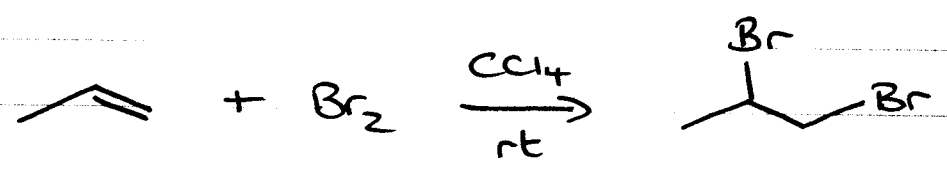
④ RADICAL STABILITY

(reflected in BDE values from last lecture)

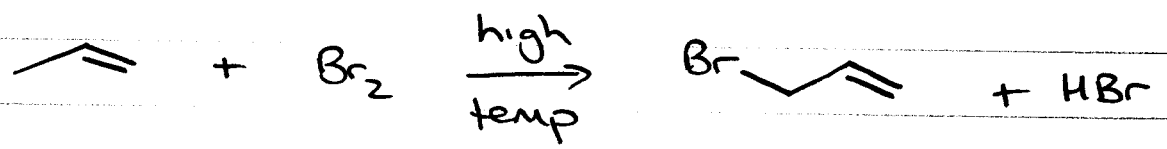


same effect as with carbocations

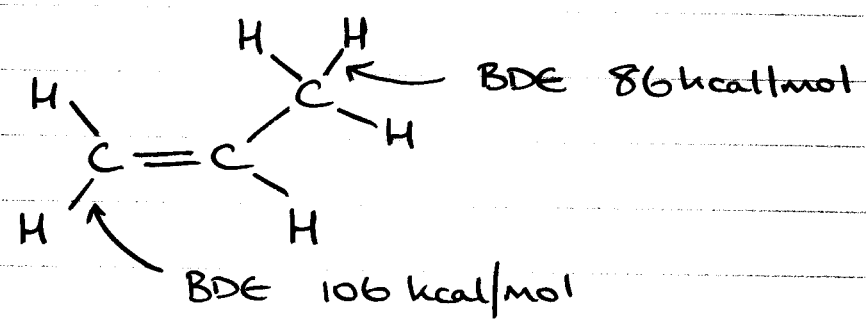
⑤ ALLYLIC HALOGENATION



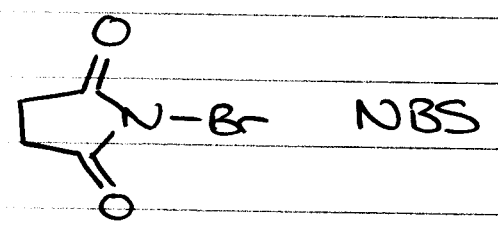
electrophilic addition



allylic substitution

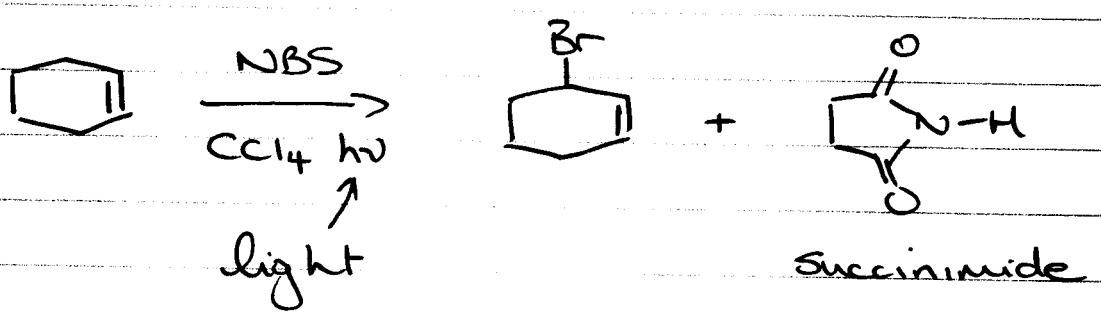


more convenient reagent

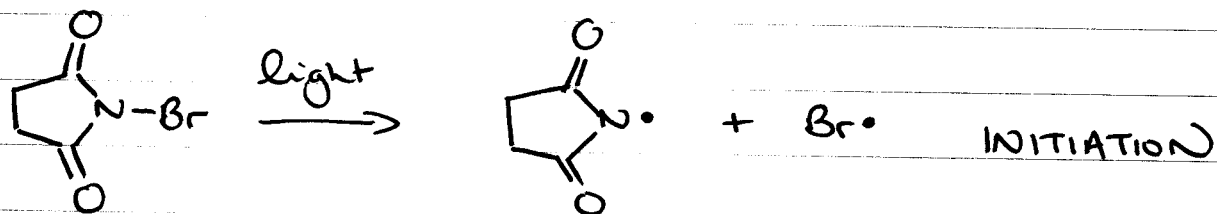


N-Bromosuccinimide

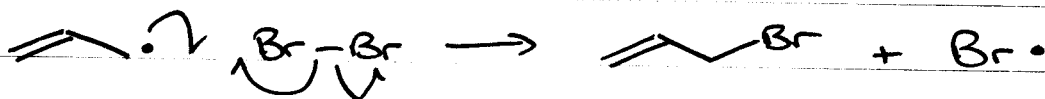
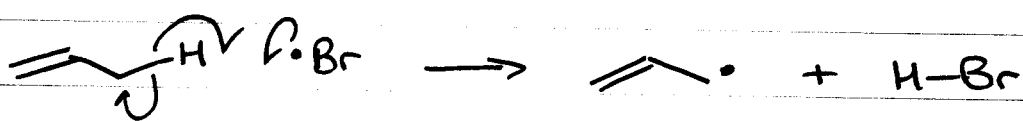
reaction can be done at room temperature



mechanism



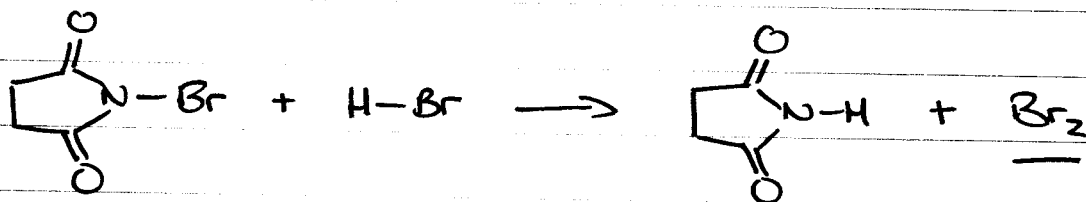
PROPAGATION



TERMINATION

- combination of 2 radical species

BUT where did Br_2 come from?



WHY DOES Br_2 not do electrophilic addition?

- LOW CONC
- RADICAL REACTIONS ARE MUCH FASTER