LEC 25 CHEM 30A Mar 14th

1. REGIOSELECTIVITY
2. BOND ENERGETICS
3. MECHANISMS
4. HAMMOND POSTULATE
5. RADICAL STRUCTURE/STABILITY
6. ALLYLIC HALOGENATION

Thurs 17th
Review Session
Young Hall 2200
Time: 1-3 pm

WEDS - Quiz 3 + EVALS
Read Ch 7
Problems 7.4, 7.5 - 7.27

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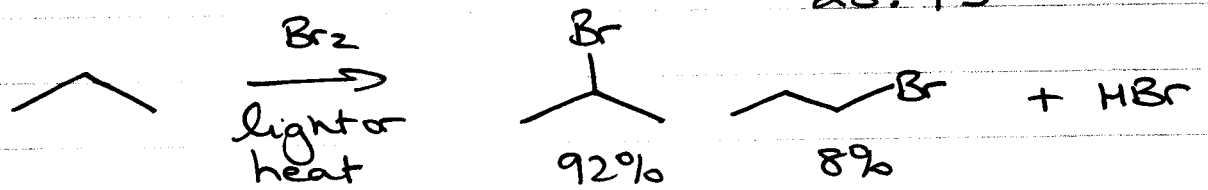
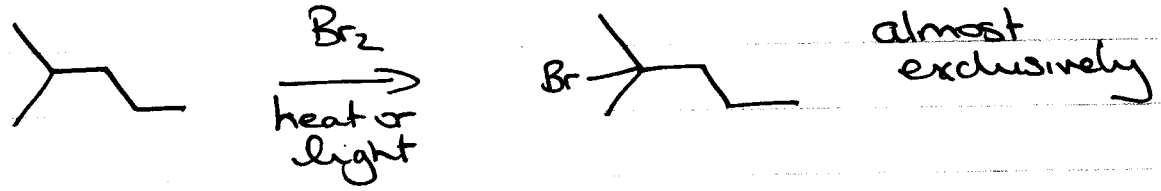
1. REGIOSELECTIVITY

(Statistics say 25:75)



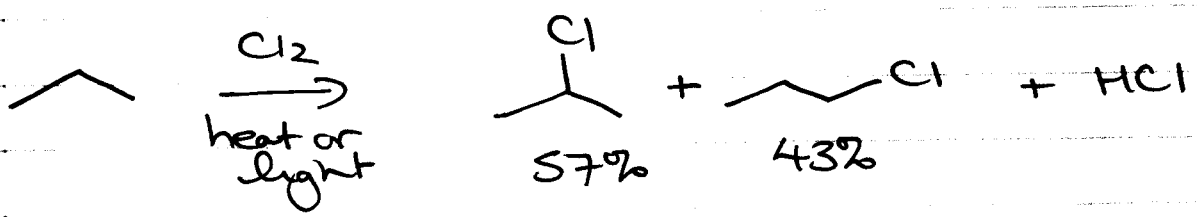
2° favored over 1° (also 3° favored over 2°)

So



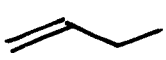
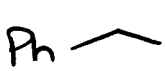
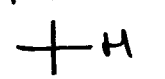
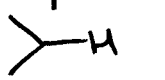
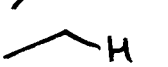
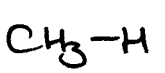
almost exclusively

REGIOSELECTIVITY LESS PRONOUNCED FOR CHLORINATION



3°/2°/1°	1600 / 80 / 1	Br
	5 / 4 / 1	Cl

(2) BOND ENERGETICS

C–H BOND		BDE (kcal/mol)
	(ALLYL)	86
	(BENZYL)	88
	(t-BUTYL)	93
	(i-PROPYL)	96
	(ETHYL)	100
CH_3–H	(METHYL)	105
	(VINYL)	106

So, consider:

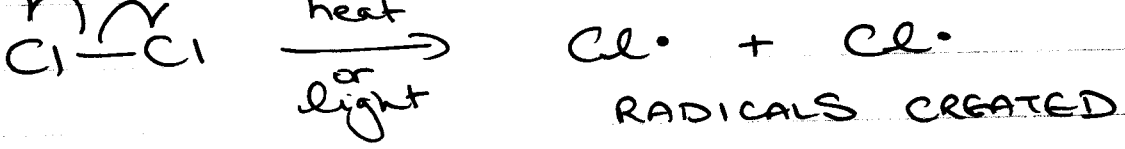
$\Delta H = -24$ kcal/mol (EXOTHERMIC REACTION)

(3) MECHANISMS

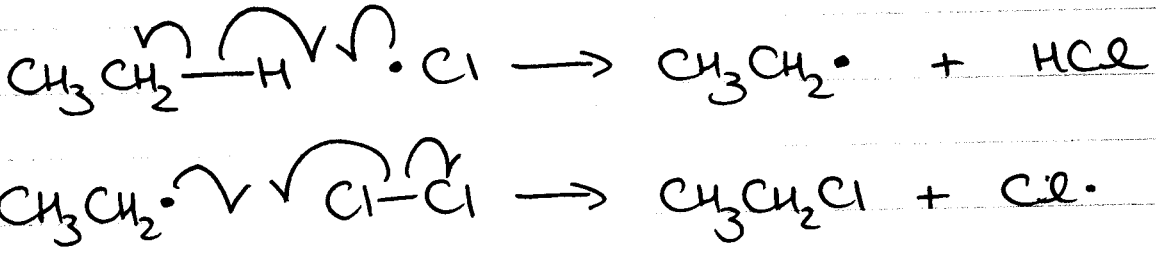
3 STEPS INITIATION / PROPAGATION / TERMINATION

e.g. $CH_3CH_3 \xrightarrow{Cl_2} CH_3CH_2Cl + HCl$

(i) CHAIN INITIATION

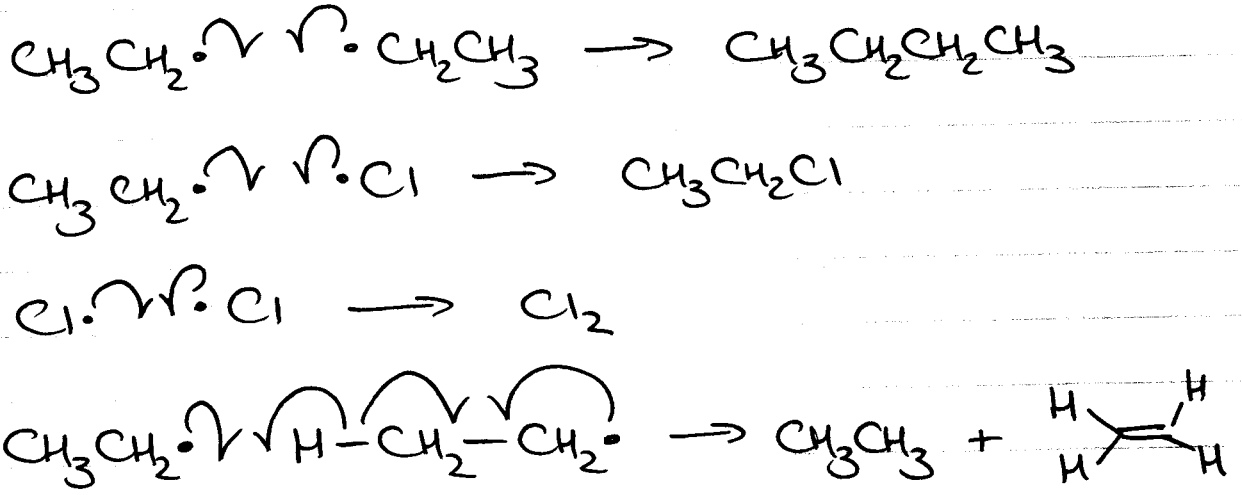


(ii) CHAIN PROPAGATION



PROPAGATES RADICALS

(iii) CHAIN TERMINATION



CONSUMES RADICALS

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

kcal/mol

$CH_3CH_2-H + Cl\cdot \rightarrow CH_3CH_2\cdot + HCl$ -3

(+100) (−103)

$CH_3CH_2\cdot + Cl-Cl \rightarrow CH_3CH_2Cl + Cl\cdot$ -21

(+59) (−80)

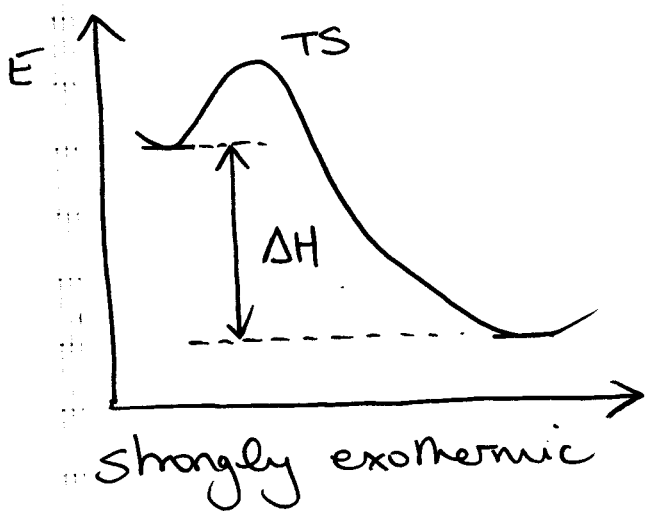
+

$CH_3-CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$ -24

Gives: reaction stoichiometry and heat of reaction (ΔH)

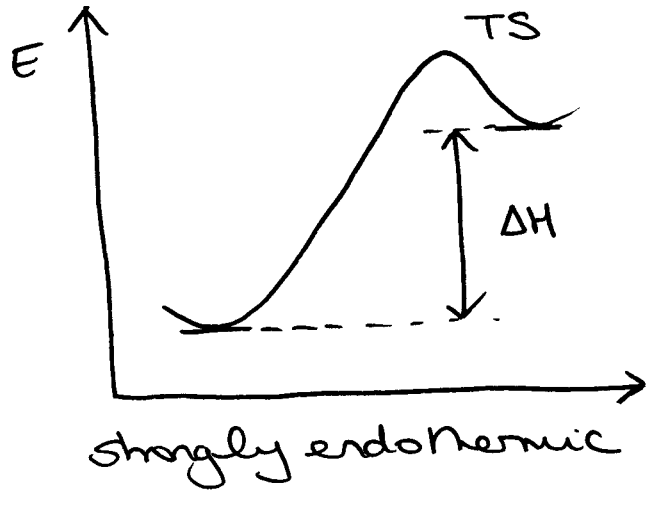
④ HAMMOND POSTULATE

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



strongly exothermic

TS looks like reactant

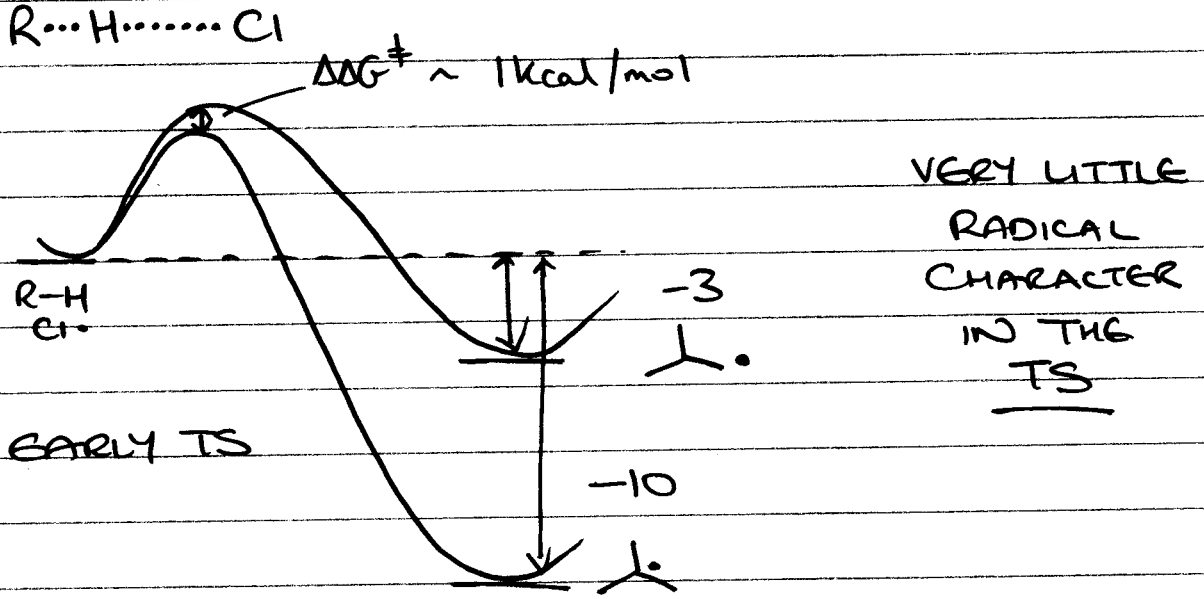


strongly endothermic

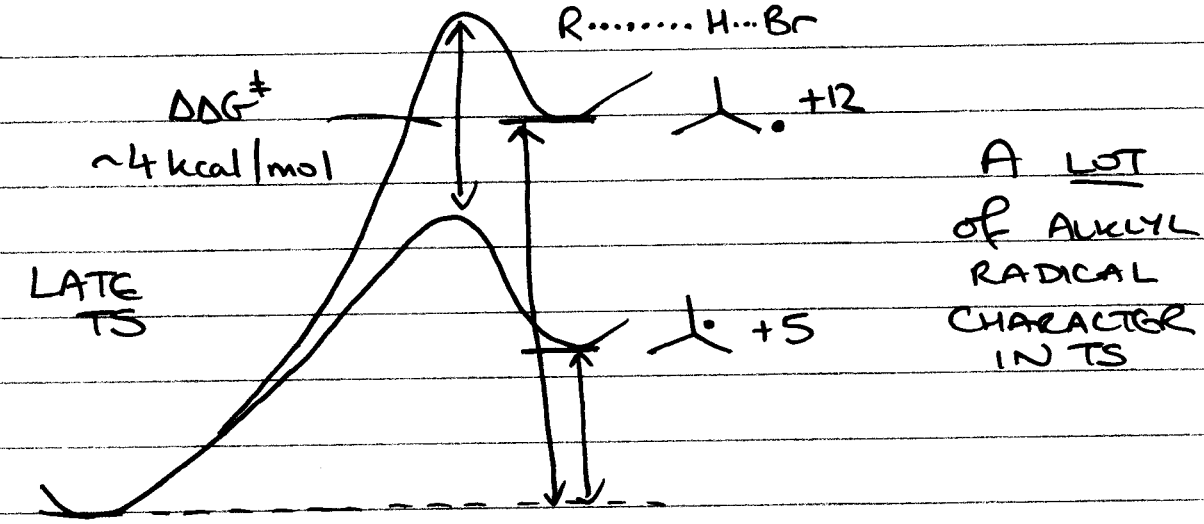
TS looks like product

- Abstraction of H is RDS, consider:

- CHLORINATION (exothermic RDS)

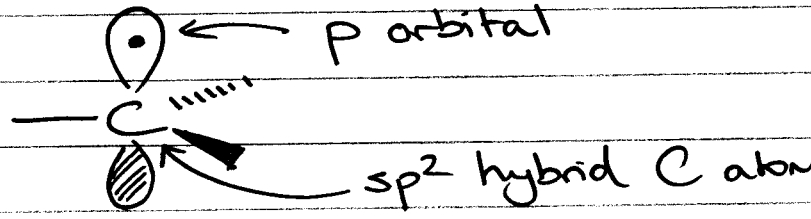


- BROMINATION (endothermic RDS)

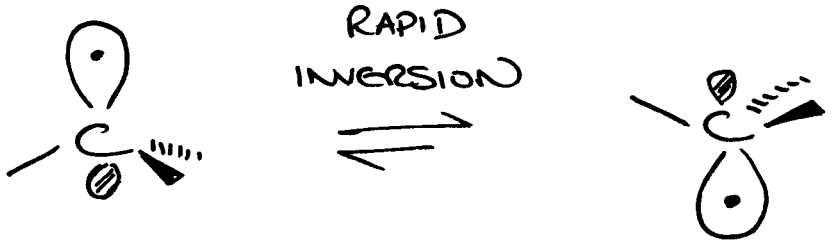


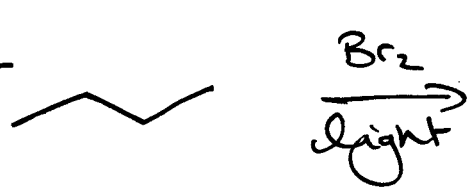
In BROMINATION, stability of radical is much more reflected in TS than in CHLORINATION, so REGIOSELECTIVITY much greater in BROMINATION

(5) RADICAL STRUCTURE

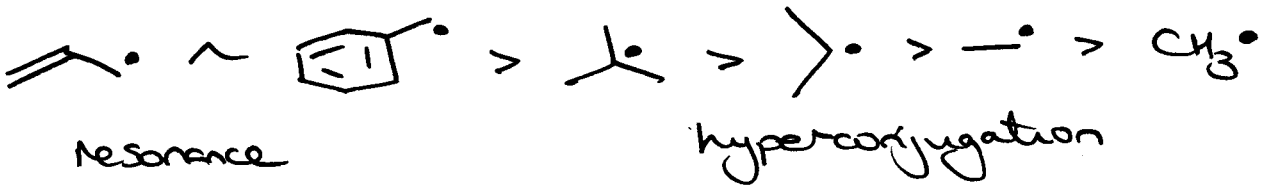


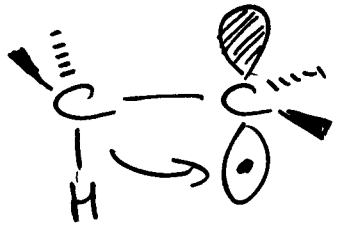
actually a Shallow Pyramid



So 

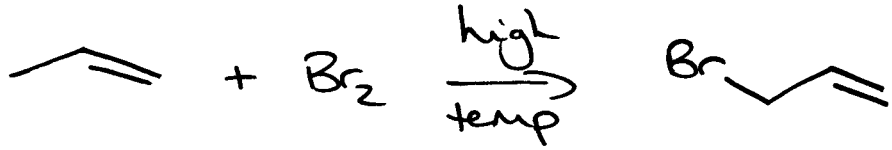
– STABILITY
(reflected in BDE values)



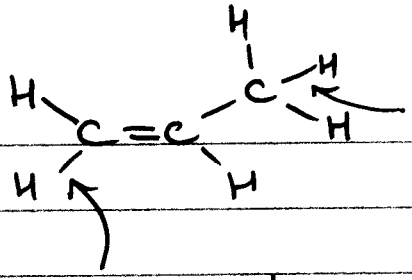


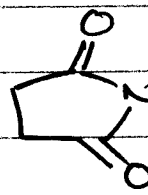
same effect as with CARBOCATIONS

(6) ALLYLIC HALOGENATION



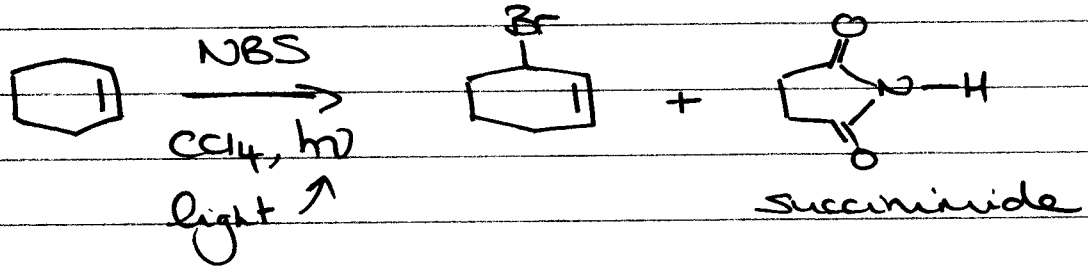
allylic substitution



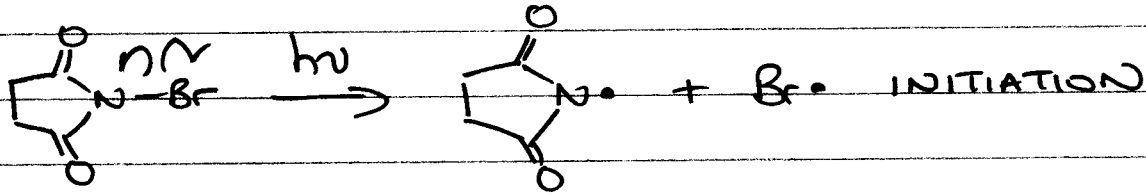
= more convenient reagent  NBS

N-Bromosuccinimide

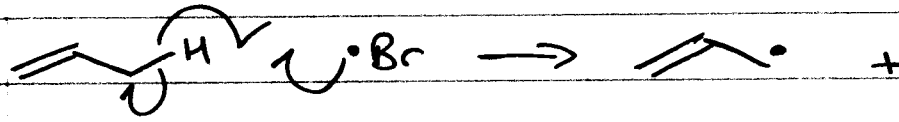
Reaction can be done at room temperature

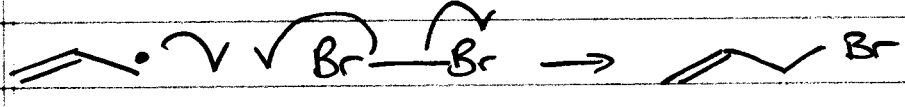


mechanism:



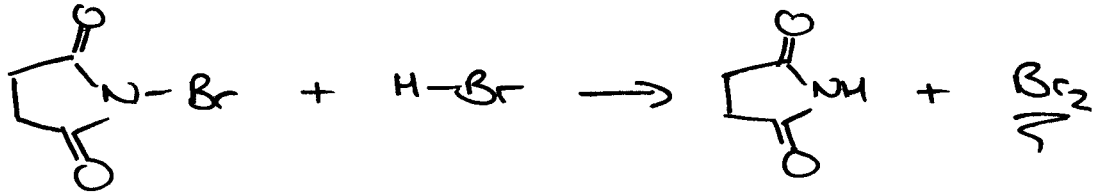
PROPAGATION





TERMINATION – combination of radicals to form non-radical species

Where did the Br_2 come from?



Why does Br_2 not do electrophilic sub?

- Low conc
- RADICAL REACTIONS ARE MUCH FASTER.