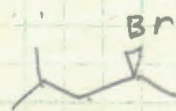


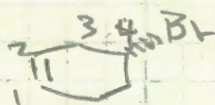
Name Haloalkanes, Halogenation, Radical Reactions



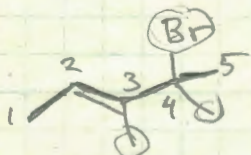
(S)-2-bromo-4-methylpentane

Why NOT

(S)-2-methyl-4-bromopentane? Alphabetical



(R)-4-bromocyclohexene



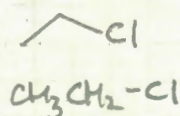
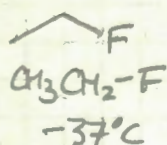
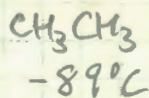
show stereoconfiguration as E/Z or R/S where needed)

(2E,4E)-4-bromo-3,4-dimethyl-2-pentene

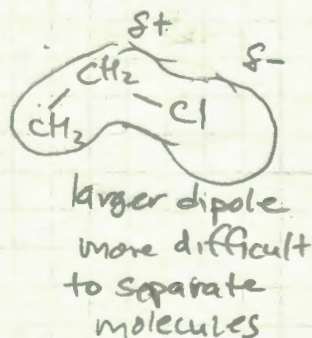
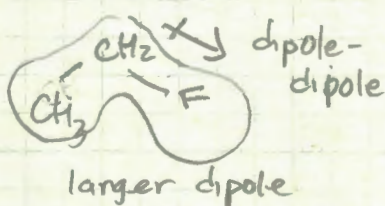
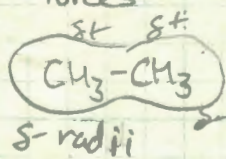
Boiling Points

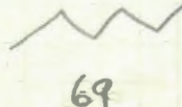
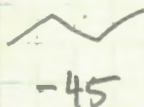
Why this trend?

bp



Van der Waals forces

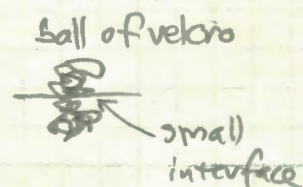


bp
°C

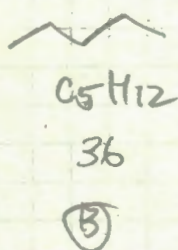
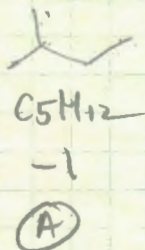
Velcro analogy



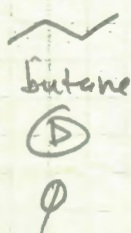
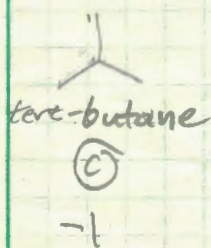
longer chain, more overlap



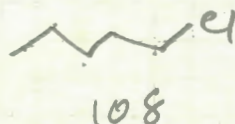
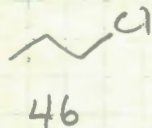
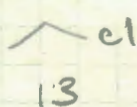
Look at



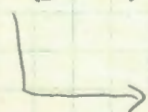
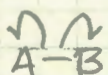
why is more E (heat) need to separate molecules of (B) than (A)

same Q as above
(C) vs (D)

Likewise, haloalkanes follow same trend w/ length.

bp
°C

Bond Dissociation Energy

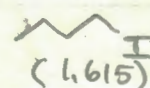
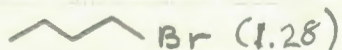
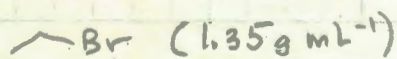


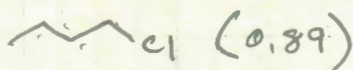
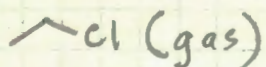
Notice half-barbed arrows denote movement of 1 electron

Energy is needed so ΔH° is > 0 (zero)

radical products

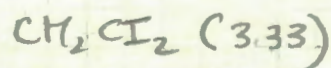
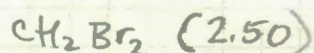
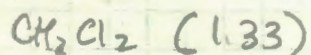
Density (mass-to-volume)

Liquid Alkyl Br and I are denser than H₂O (1.0 g mL⁻¹)



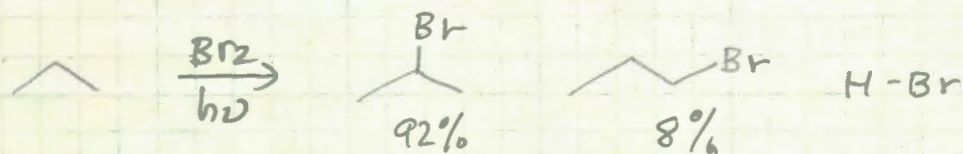
not liquified at
25°C, 1 atm Press.

As more X's added the mass-to-volume ratio ↑
density exceeds that of H₂O.

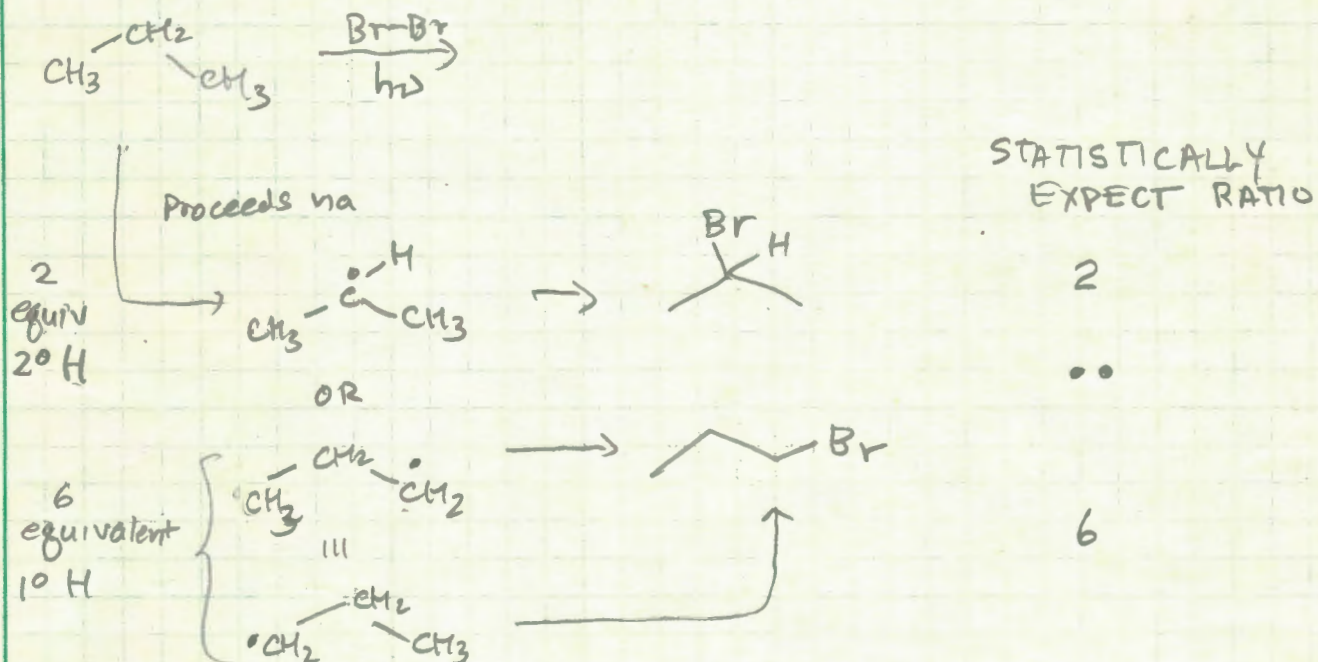


	BDE (kcal mol ⁻¹)	bond length (pm) ^{10⁻¹² meters}
C-H → $\cdot\text{C}\cdot$ $\text{H}\cdot$	+99	109
C-F → $\cdot\text{C}\cdot$ $\text{F}\cdot$	+111	 longer
C-Cl → $\cdot\text{C}\cdot$ $\text{Cl}\cdot$	+85	
C-Br → $\cdot\text{C}\cdot$ $\text{Br}\cdot$	+78	
C-I → $\cdot\text{C}\cdot$ $\text{I}\cdot$	+57	214

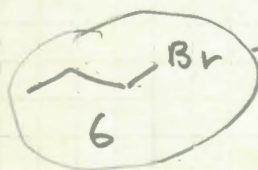
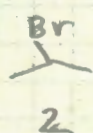
Regioselectivity of Radical halogenation



What you expect



That is



Expected to be more abundantly made!
Why is it not?

$\frac{2}{8}$
 ||

25%

92%

$\frac{6}{8}$
 ||

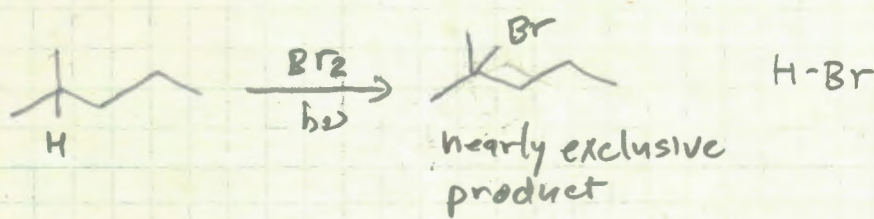
75% expected

8% observed

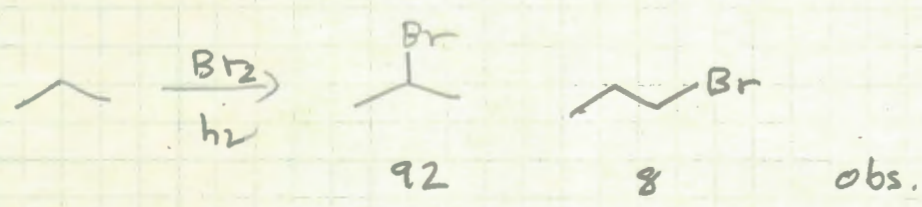
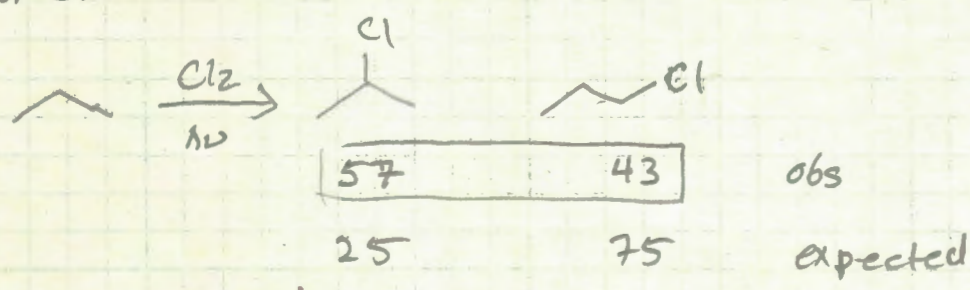
$H \rightarrow Br$ replacement is favored for $2^\circ H$ over $1^\circ H$

Actually

$3^\circ H > 2^\circ H > 1^\circ H$ for replacement by Br



For Cl

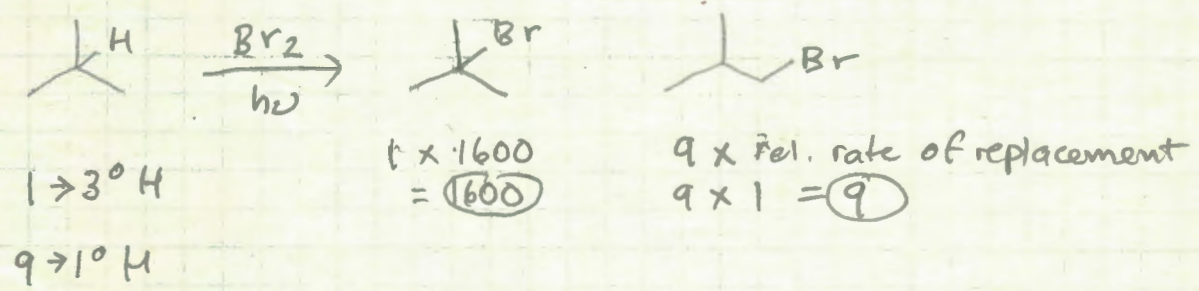


Br_2 is far more regioselective than Cl_2 in monohalogenation

The regioselectivity per hydrogen of bromination for

$3^\circ H$	$2^\circ H$	$1^\circ H$	replacement is
1600	80	1	

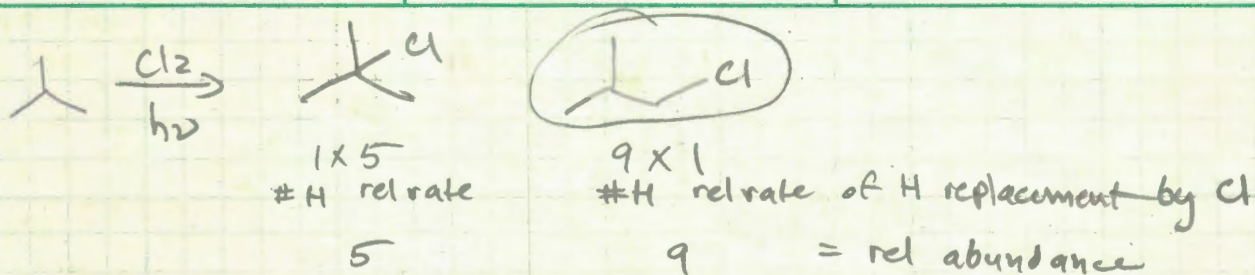
$\therefore$



relative abundance 1600 to 9

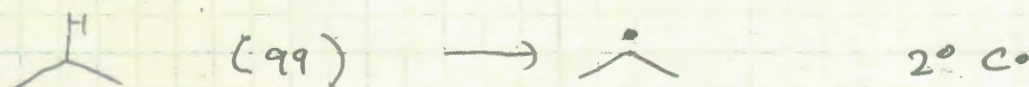
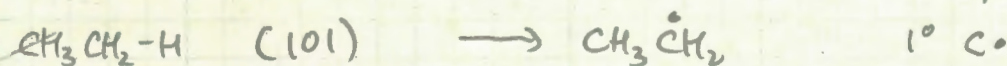
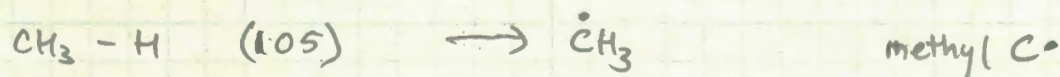
The regioselectivity per hydrogen of chlorination for

$3^\circ H$	$2^\circ H$	$1^\circ H$
5	4	1



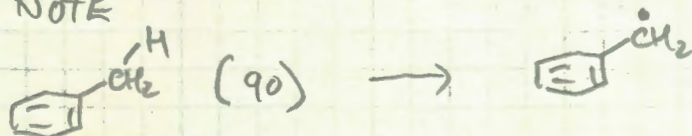
MORE ABUNDANT CIRCLED

BDE of 1°, 2°, 3°, methane Hydrogens

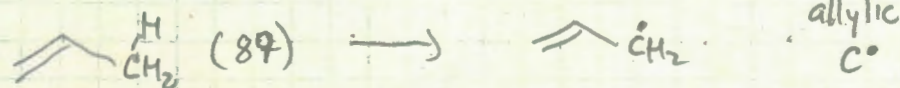


Lowest BDE
 ∴ easier to form because radical is more stable

NOTE



benzylic C•

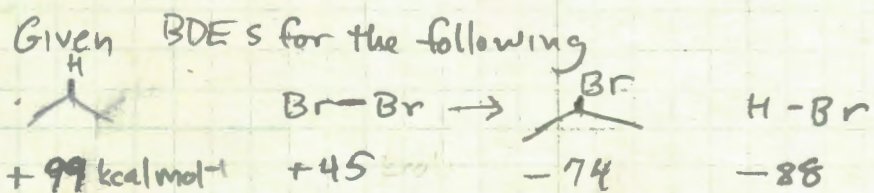


allylic C•

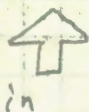
NOTE these follow the same order of stability as C⁺

3° C⁺ more stable than 2° C⁺ > 1° C⁺ > methyl C⁺

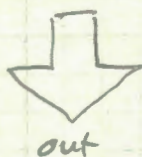
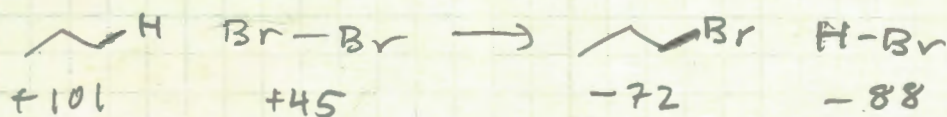
Let's look at ΔH° values to assess the energetics of bromination regioselectivity.



+144



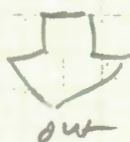
-162

system $\Delta H^\circ = -18 \text{ kcal/mol}$ 

+146

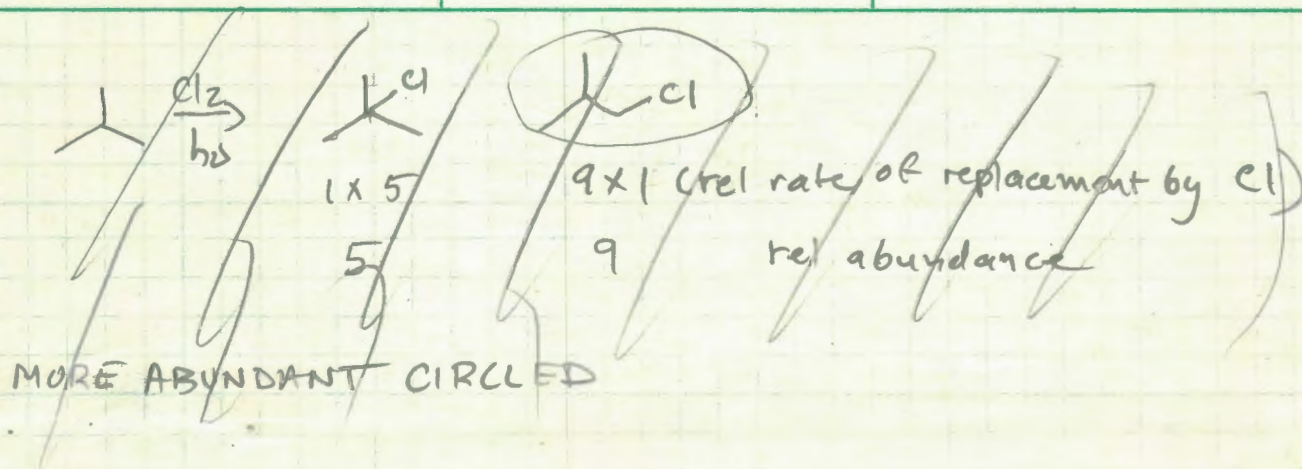


-160

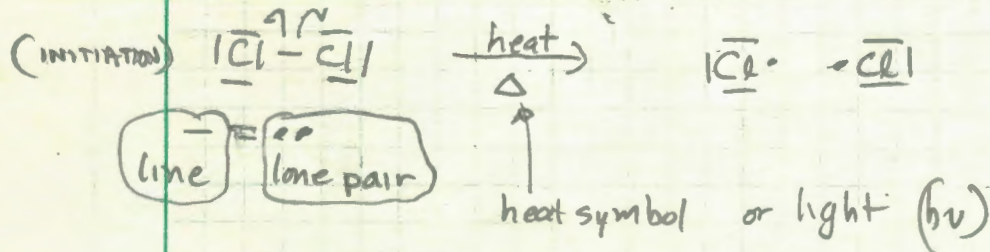


-14 kcal/mol

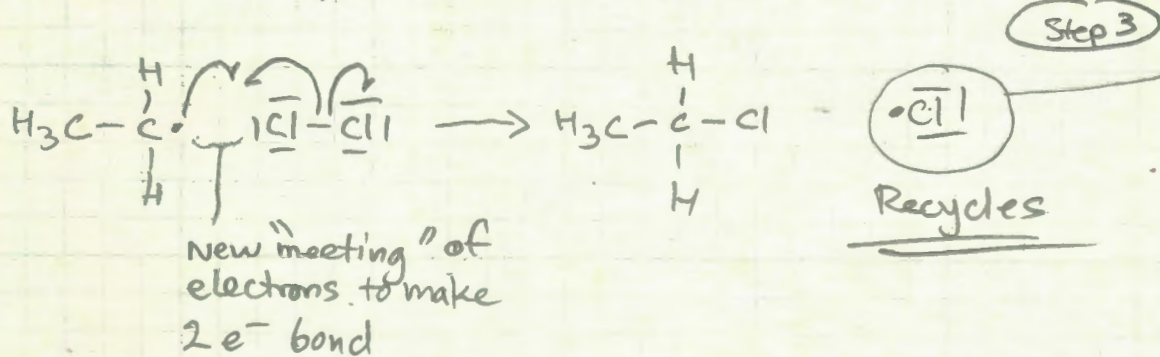
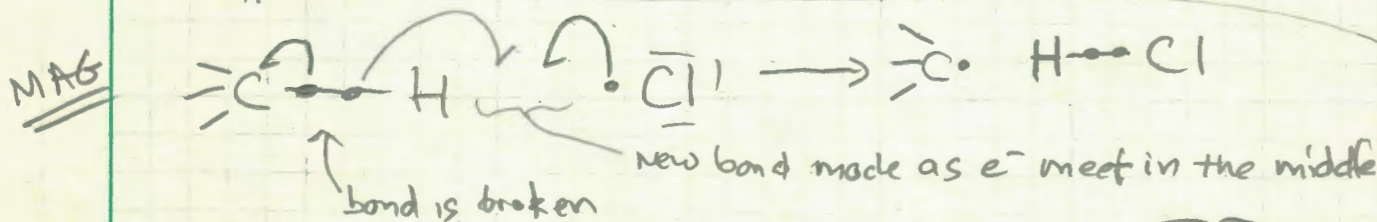
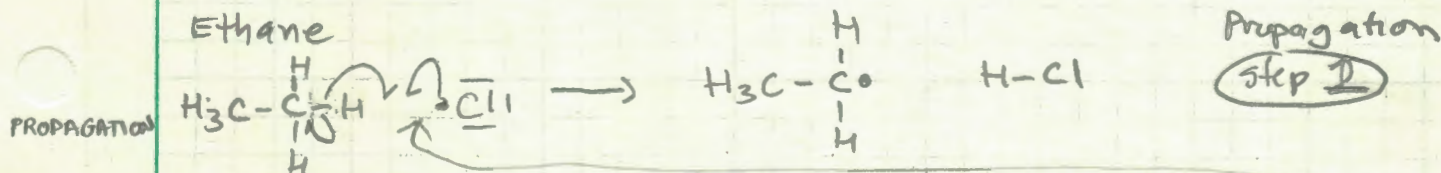
less exothermic
than previous2^o example above



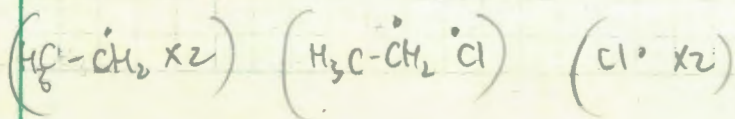
How to Make Chloroalkanes



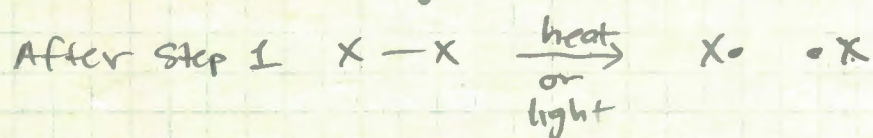
Initiation
 Step 1
 half-barbed arrow movement of 1 e^-



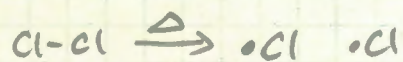
Chain termination steps are any where 2 radicals joins and make no NEW RADICALS. For example



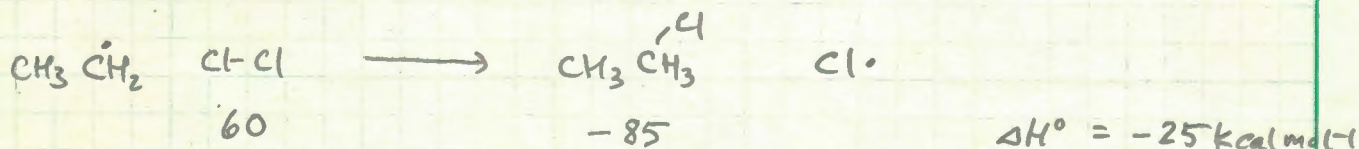
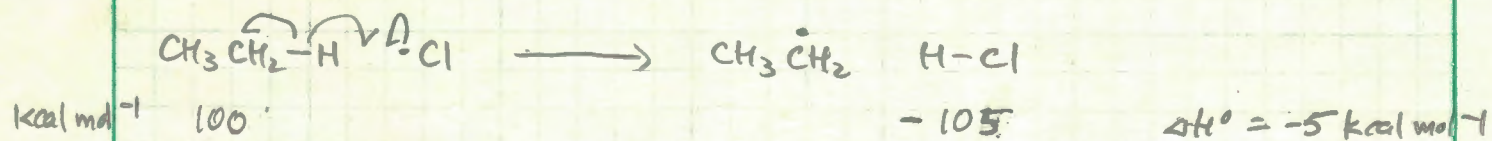
Energetics of Propagation Steps



the reaction progresses based on the heat of reaction (ΔH°) of the propagation steps



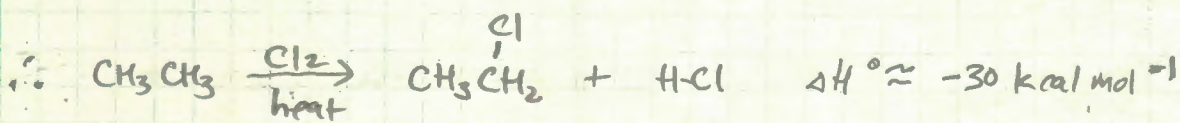
step 2



sum

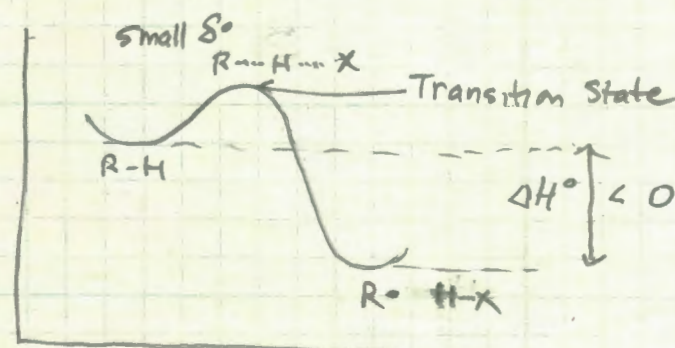
$$\Delta H^\circ = \underline{-30 \text{ kcal mol}^{-1}}$$

for propagation steps



Hammond Postulate explains the character of the transition state radicals ($R\cdot$).

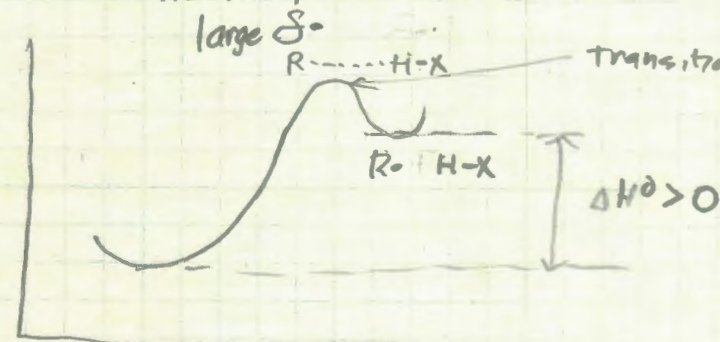
Exothermic Rxn



i.e. PRE-radical formation

RELATIVE RADICAL STABILITY
DOES NOT INFLUENCE
PRODUCT YIELD

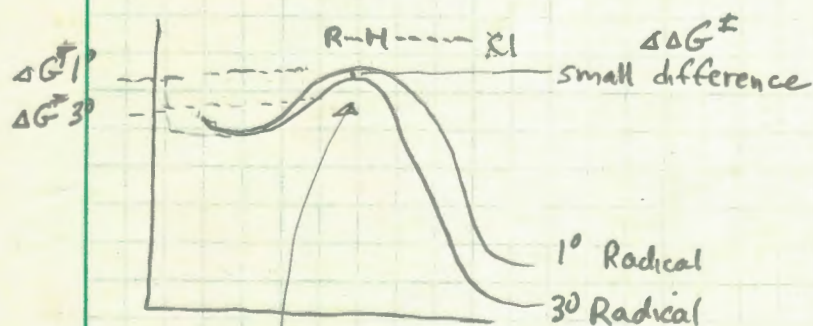
Endothermic Rxn



(in this case radicals ($R\cdot + H\cdot$))

REL RADICAL STABILITY
INFLUENCES RXN RATE
DICTATED BY TS ENERGIES

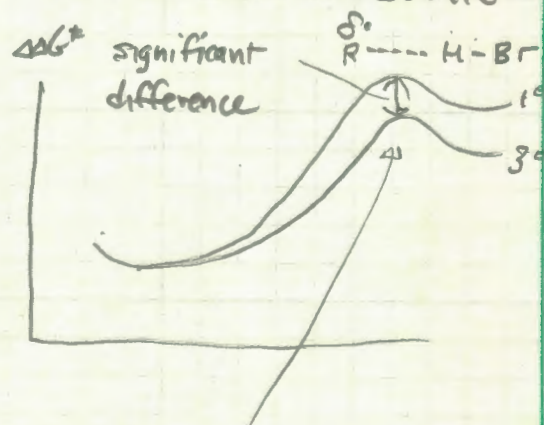
R-H + Cl (Exothermic)



Similar TS Energies Suggest

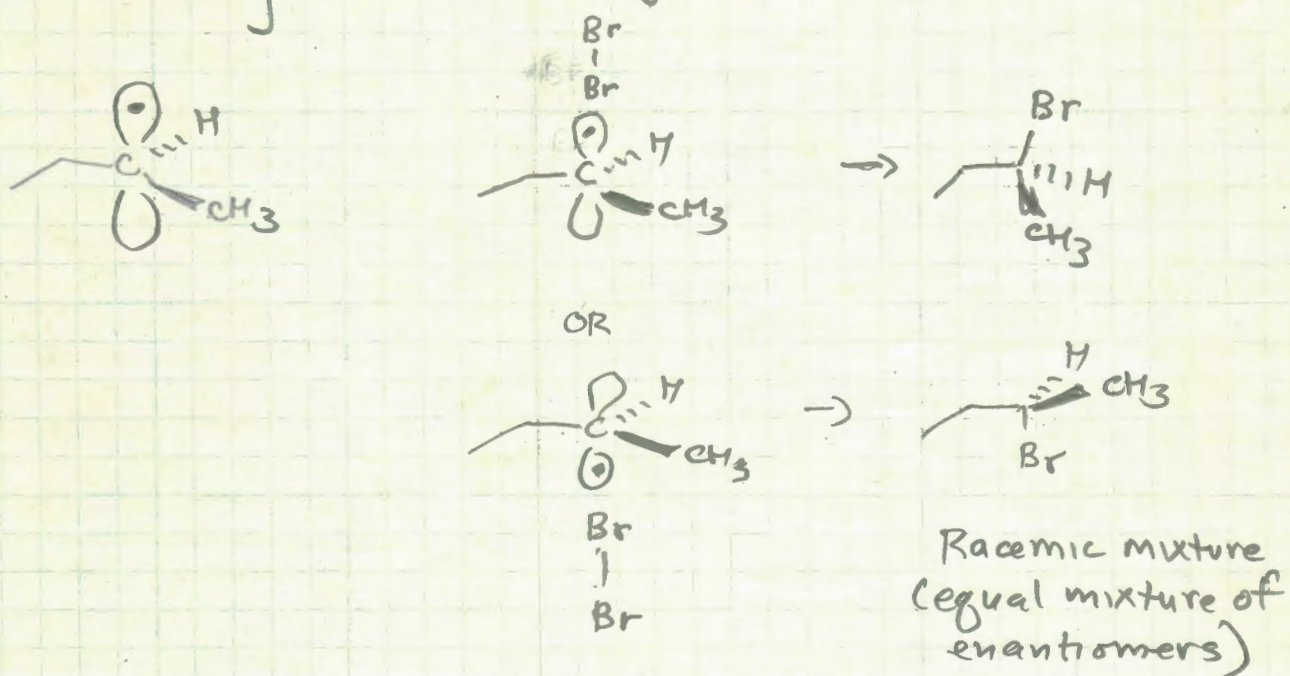
1° and 3° Radicals are made
at similar abundances by $Cl\cdot$
H-abstraction
(removal)

R-H + Br Endothermic

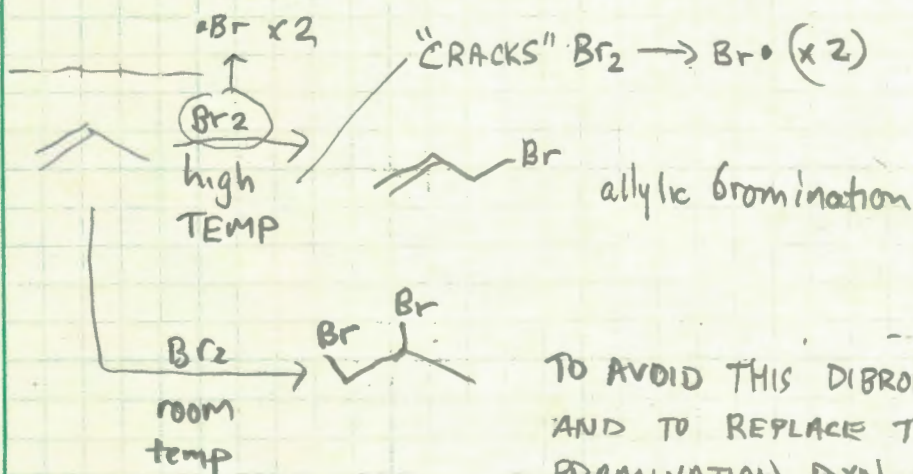
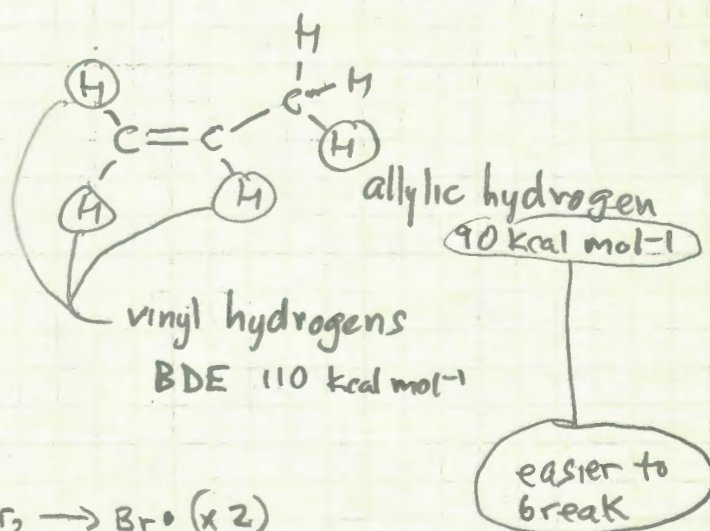
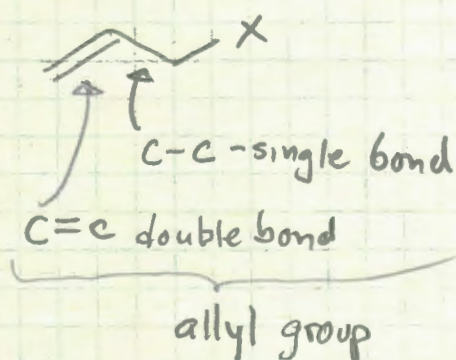


Vastly different TS Energies
Suggest 1° and 3° Radicals
are made a significantly
different abundances by $Br\cdot$
H-removal
(abstraction)

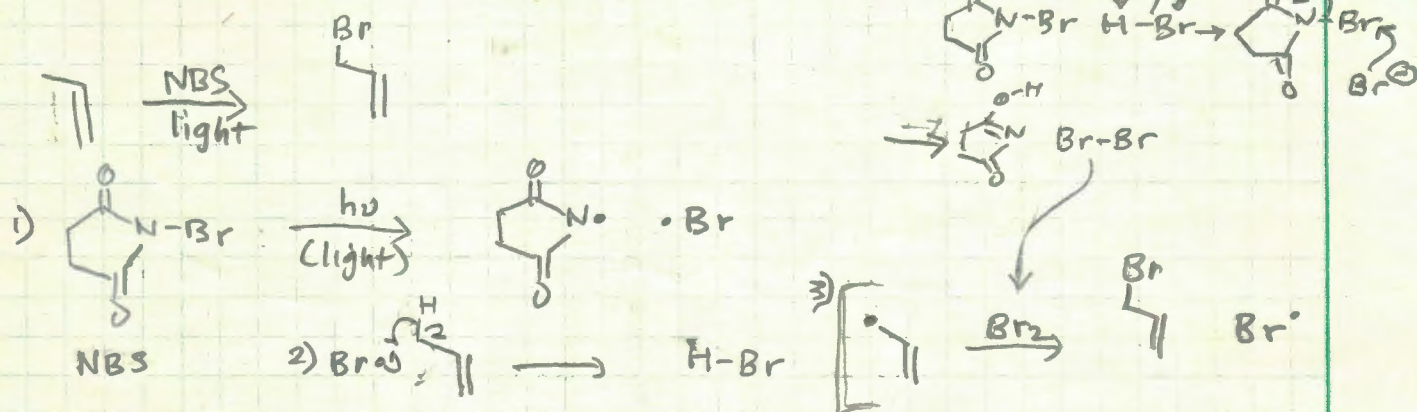
Stereochemistry of Radical Halogenation



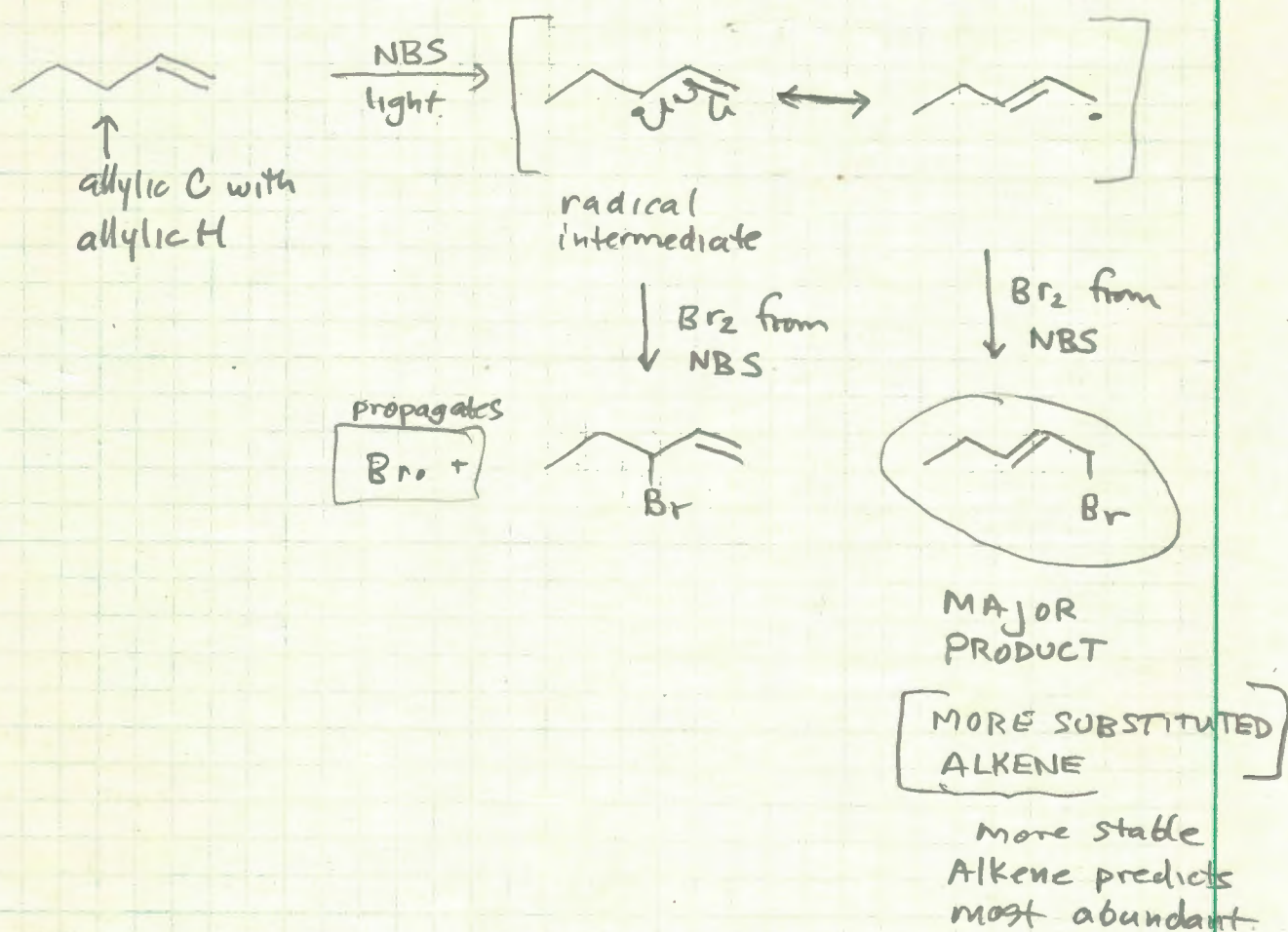
Allylic Halogenation



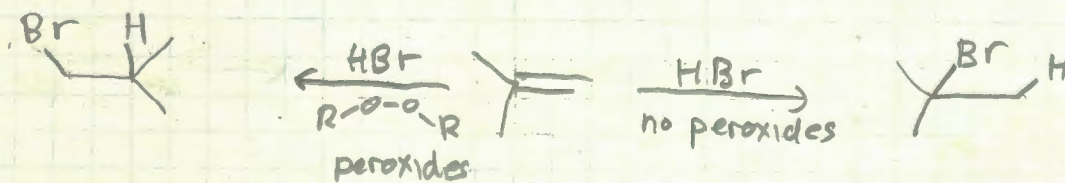
TO AVOID THIS DIBROMINATION AT ROOM TEMP
AND TO REPLACE THE HIGH TEMP ALLYLIC
BROMINATION RXN ABOVE
N-bromosuccinimide (NBS) is used

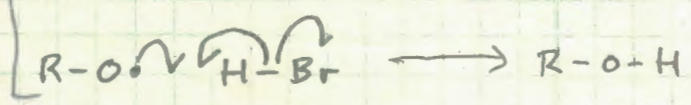
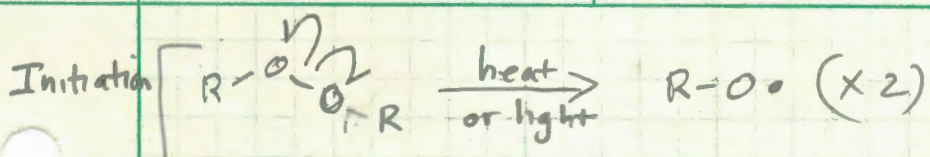


Sometimes allylic Bromination gives a mixture of unique products due to resonance.



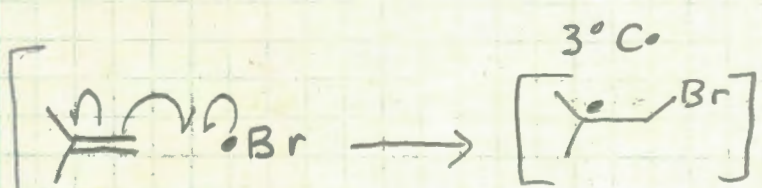
Addition of H-Br to Alkenes in Presence of Radicals.



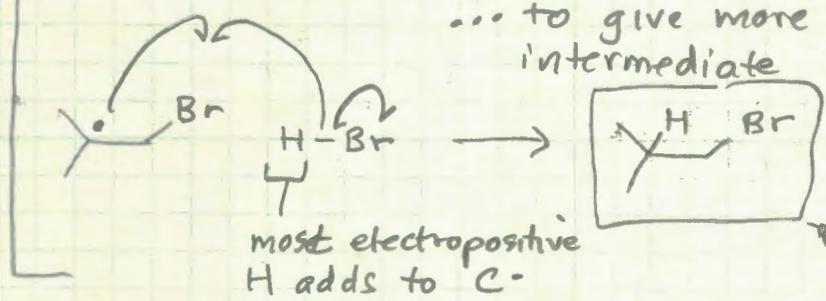


$\text{Br}\cdot$
electron deficient
acts as Lewis Acid
with Alkene...

Propagation



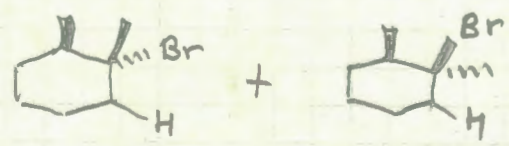
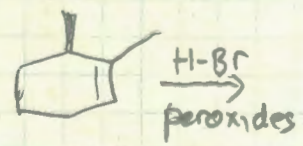
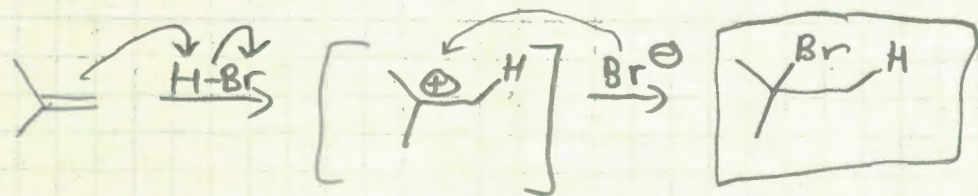
... to give more stable radical intermediate



NON-Markovnikov product.

Compare

Compare C^+ -based HBr Addⁿ to Alkene



mixture of diastereomers
No Fixed stereoselectivity.