

SECTION 9 – ALKYL HALIDES (R-X)

9-1 -- Preparation of Alkyl Halides from Alkanes

- Chlorination Reaction (Cl_2) - Unselective
- Bromination Reaction (Br_2) – Much More Selective

9-1 -- Why is Bromination Easier to Control than Chlorination?

- Radical Stabilization
- Thermochemistry of Bromination and Chlorination Reactions
- Analysis of Transition States

9-4 -- Allylic Hydrogens

- Resonance-Stabilization of the Allylic Radical
- Allylic Bromination and the Use of NBS
- Reactants that Produce 2 Types of Allylic Radicals

9-6 -- Benzylic Hydrogens

- Low Bond Dissociation Energy (BDE)
- Most Favorable Resonance Structure Preserves the Aromatic Ring
- Benzyl Radicals

9-7 -- Preparation of Alkyl Halides from Alcohols

- Via the Addition of HX
- Via the Use of Thionyl Chloride (SOCl_2) in Pyridine Solvent
- Via the Use of Phosphorus Tribromide (PBr_3)

9-8 -- Organometallic Compounds

- Carbon-Metal Bonds (Organometallics)
- Carbanions
- Grignard Reagents
- Organolithium Reagents (the Alkyl lithium Reagent)
- Organocopper Reagents (the Lithium Dialkyl Copper Reagent)

9-10 -- Various Ways to Form New C-C Bonds

- Formation of New C-C Single Bonds (σ -bonds)

Section 9 = Alkyl Halides.

9-1

↳ prepared by:

- ① halogenation of alkanes. (pg. 9-1)
- ② from alcohols via several methods. (pg. 9-7)

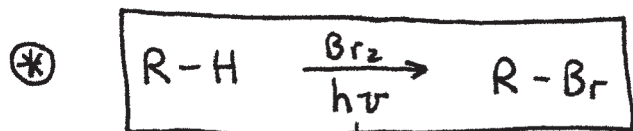
① Preparation of Alkyl Halides from Alkanes.



↳ starts reaction with radical initiators, RO-OR

↳ hard to control

↳ chlorination is difficult to control and mixtures of mono-, di-, and tri-chlorides often result.



↳ needs no initiators.

↳ bromination is easier to control.

- Why is bromination easier to control?

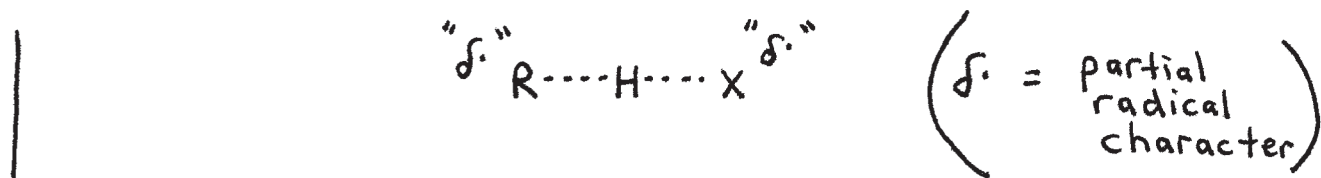
↳ Because thermochemistry affects the selectivity of a reaction.



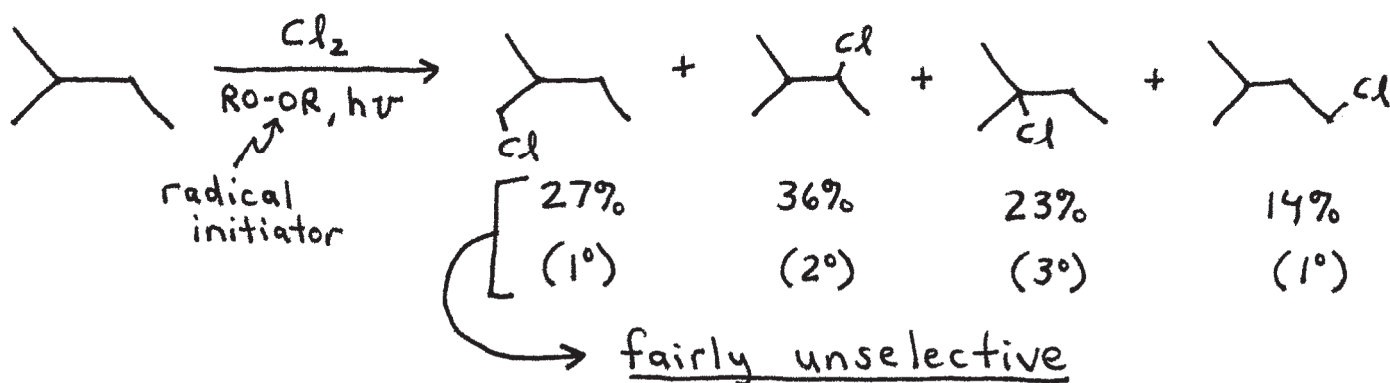
⚡
⊛ note: 3° C-H bonds react fastest, then 2° C-H bonds, and then 1° C-H bonds. H₃C-H bond reacts slowest.

↳ R· more stable, so reacts fastest. Why?....

... Because \boxed{R} requires some radical character 9-2 in the transition state:



Therefore, stabilization of \boxed{R} radical being formed, lowers the transition state also.



summary:

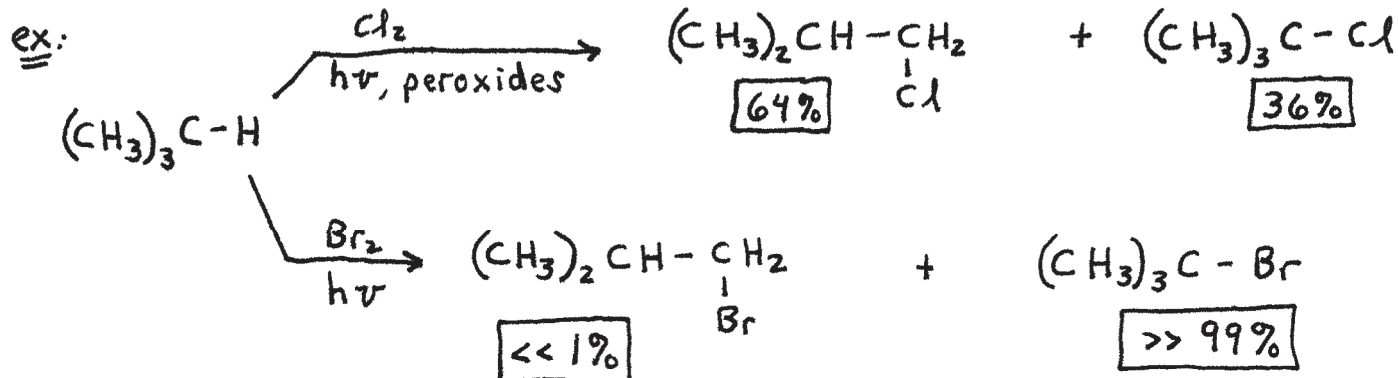
	1° C-H	2° C-H	3° C-H
total rxn.	41%	36%	23%
# H's	9	2	1
% rxn. per H	4.5	18	23

No major preference, so unselective!

relative reactivities:

1 : 4 : 5
(1°) (2°) (3°)

- chlorination is unselective while bromination is much more selective:



* relative reactivities:

9-3

	<u>1° C-H</u>		<u>2° C-H</u>		<u>3° C-H</u>
Cl.	1	:	4	:	5
Br.	1	:	200	:	19,000

Br. abstracts H. to form most stable radical only, while Cl. abstracts H. from all positions.



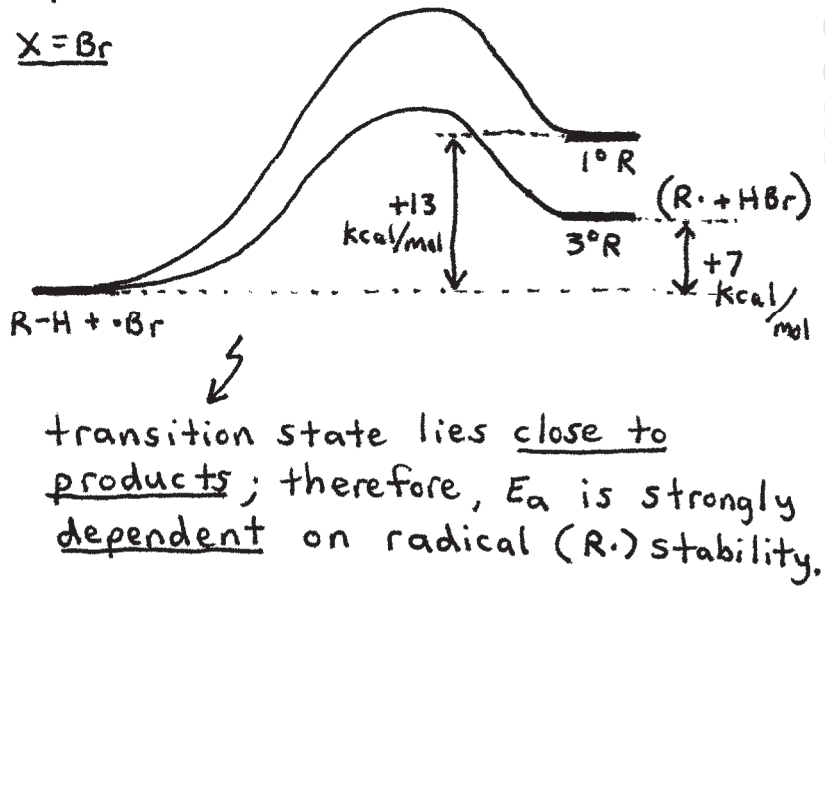
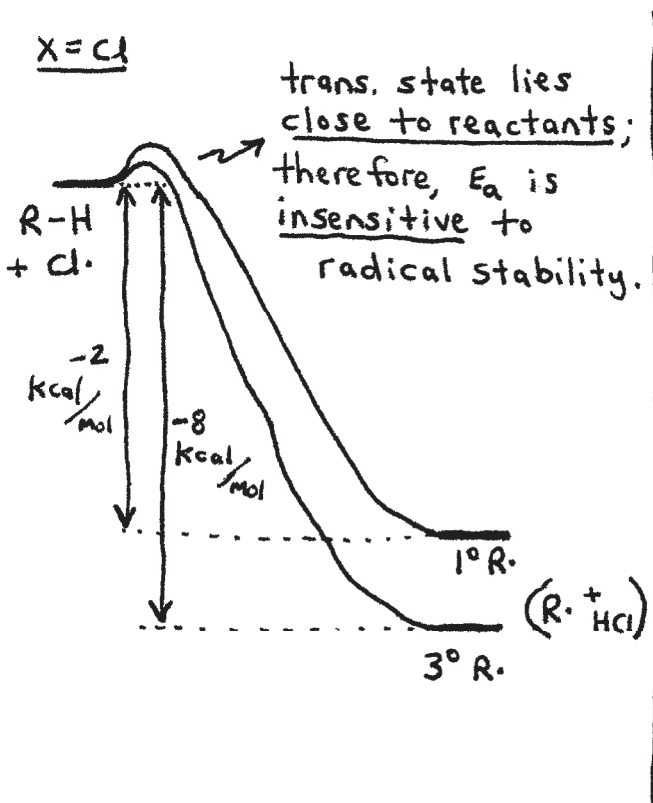
Why? ⇒ Look at the thermochemistry...

... 1st propagation step =



- involves an $\cdot H$ abstraction
- $X = Cl \rightsquigarrow \Delta H = -2$ to -8 kcal/mol
- $X = Br \rightsquigarrow \Delta H = +13$ to $+7$ kcal/mol
- ΔH 's above are for the 1st propagation step, not the overall halogenation reaction.

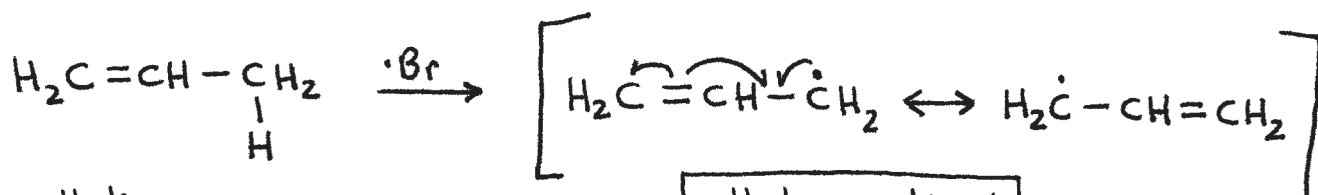
** → $\cdot H$ abstraction step:



* Note: overall, reaction in both gases (Cl_2 and Br_2) ⁹⁻⁴ is exothermic, but above "1st preparation step" (previous page) determines selectivity.

only 1 step in overall halogenation reaction.

* Allylic and Benzylic H's are especially reactive, because when an $\cdot\text{H}$ is abstracted, they form very stable radicals:

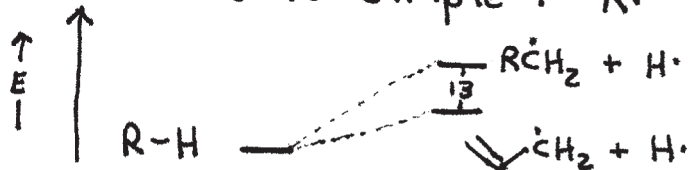


allylic



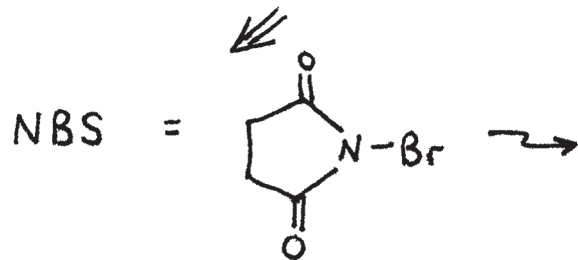
C-H BDE = 88 kcal/mol is low, so easily broken.

allylic radical = resonance stabilized by 13 kcal/mol relative to simple 1° R.

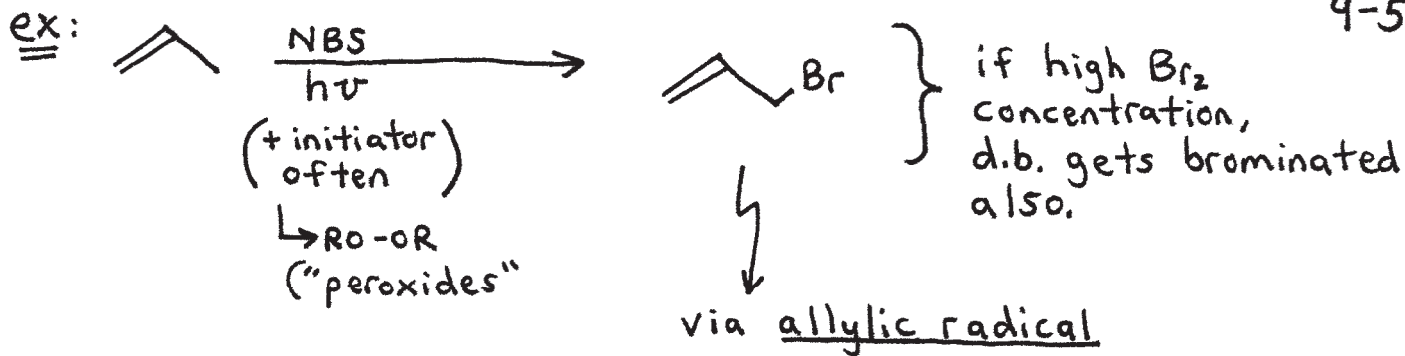


* careful: when concentration of Br_2 is high, its addition to the double bond is a problem if one's trying to do allylic bromination.

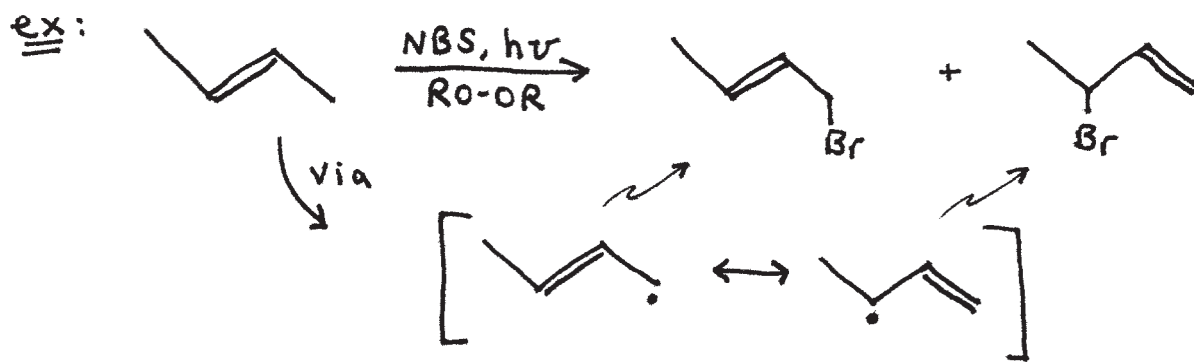
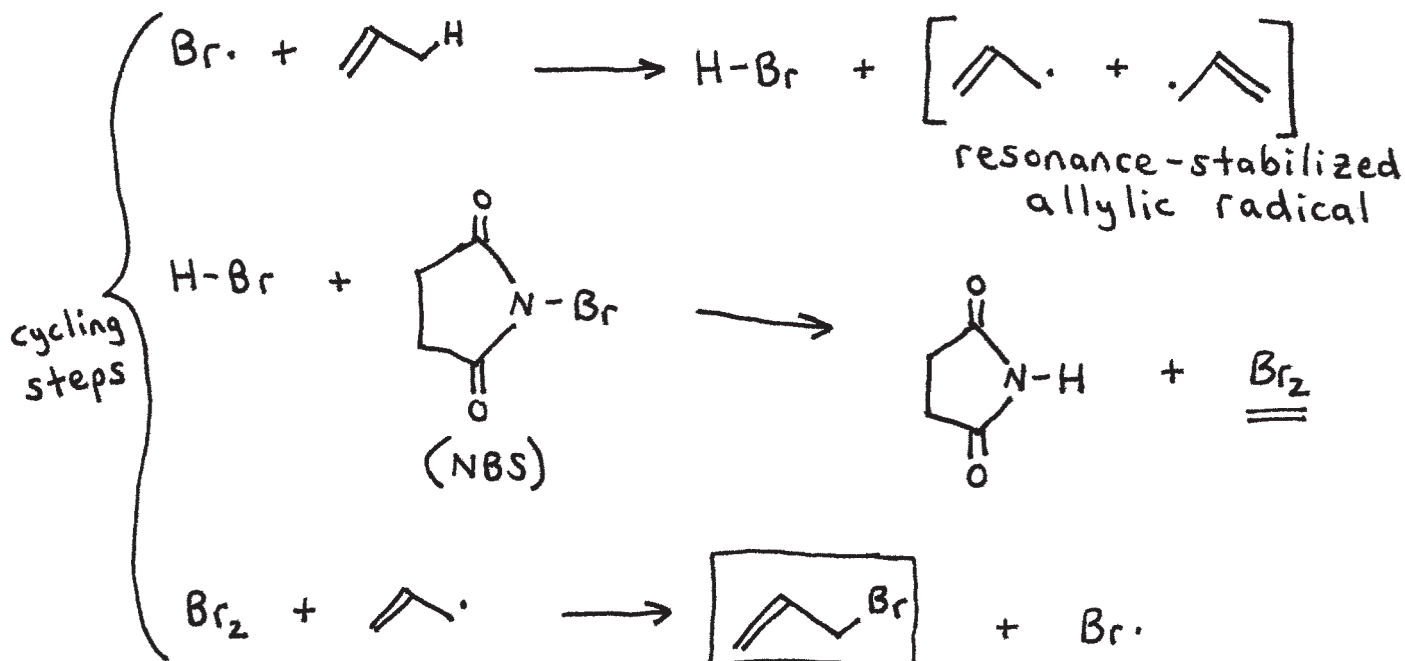
↳ low Br_2 concentration gives good allylic bromination; use N-bromosuccinimide (NBS) as source of " $\cdot\text{Br}$ "



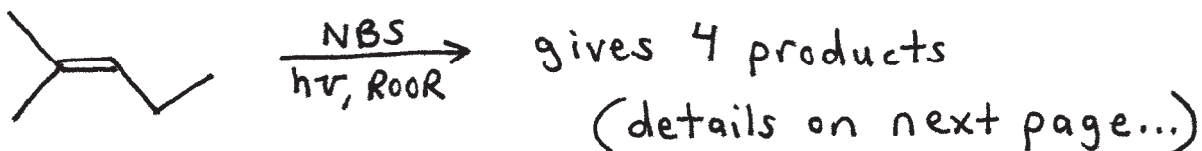
reacts with H-Br produced in reaction to form Br_2 in low concentration as reaction proceeds.



mechanism: propagation steps:



ex: more complicated; involves 2 types of allylic radicals.



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