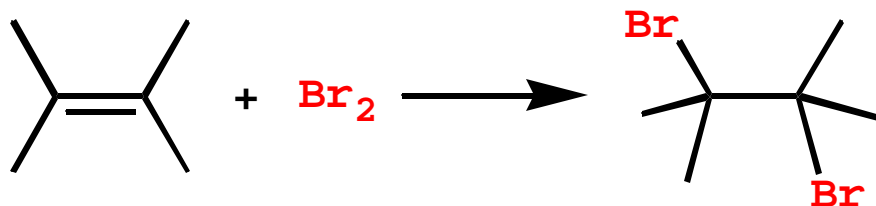


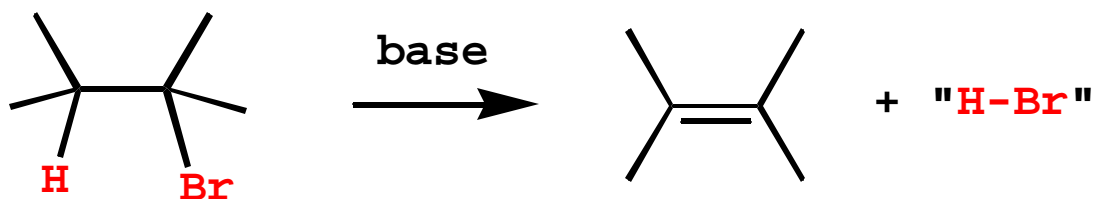
Chapter 5 - Overview of Organic Reactions*

*Four major reaction types...

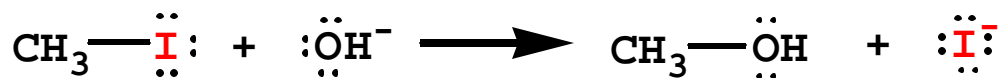
1. Addition...



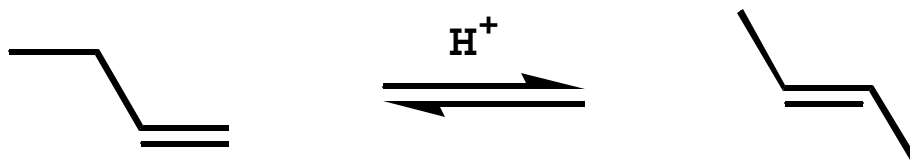
2. Elimination...



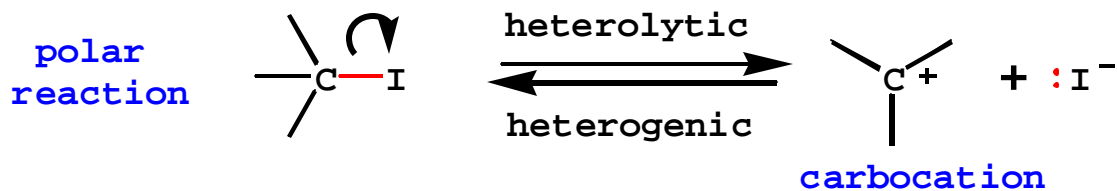
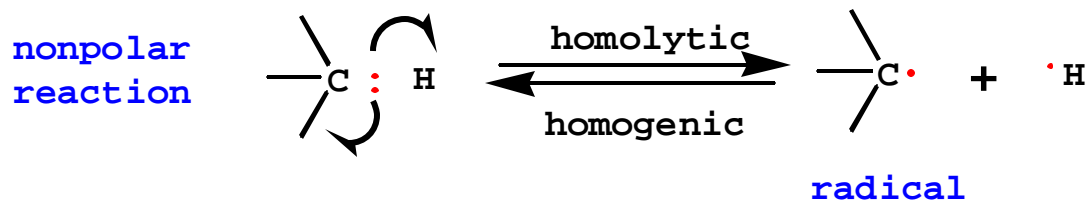
3. Substitution...



4. Rearrangement...

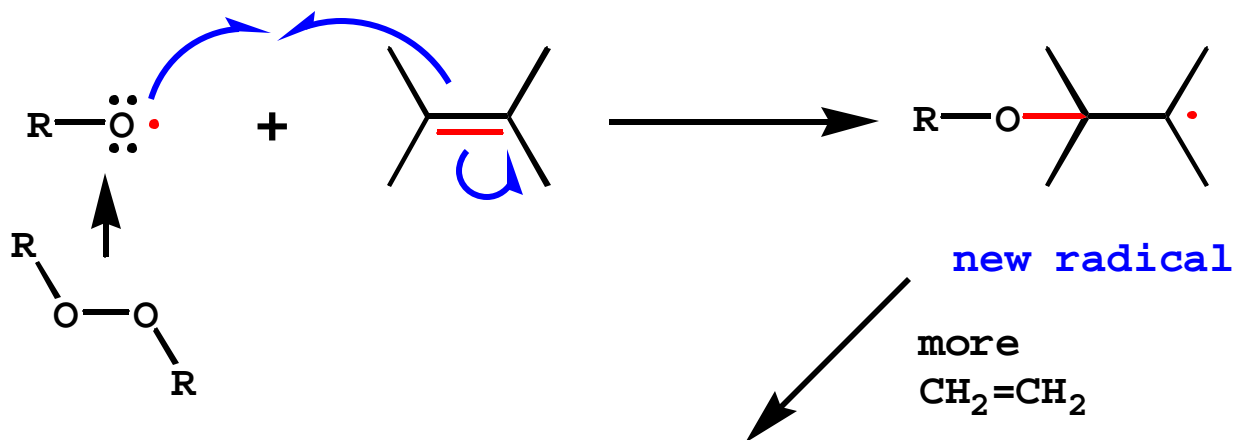


*Two general kinds of bond breaking..



*Two general kinds of radical reactions..

1. Addition..



for $\text{CH}_2=\text{CH}_2\dots$
 $T = 100-200^\circ$,
 $P > 1000 \text{ atm}$

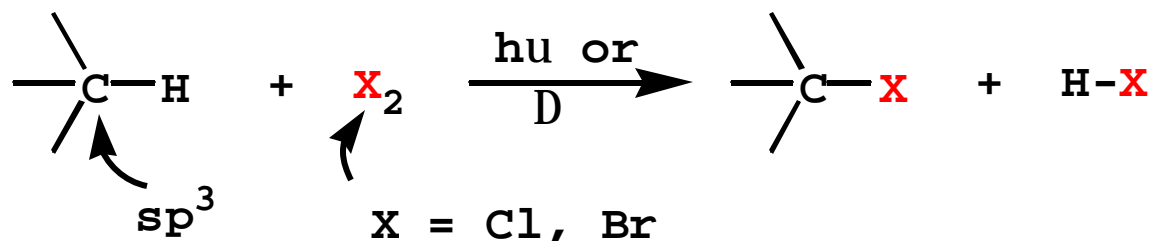
$-(\text{CH}_2-\text{CH}_2)_n-$

more
 $\text{CH}_2=\text{CH}_2$

2. Substitution...

alkanes \rightarrow alkyl halides
example of a chain reaction

Overall reaction...

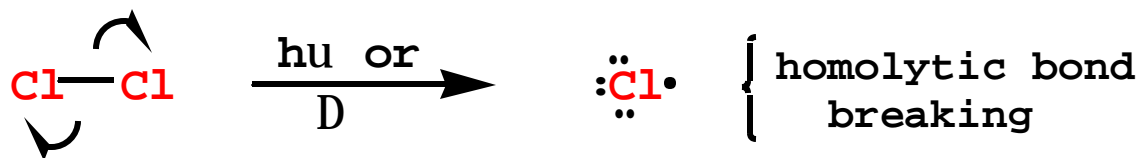


Mechanism has 3 major steps...

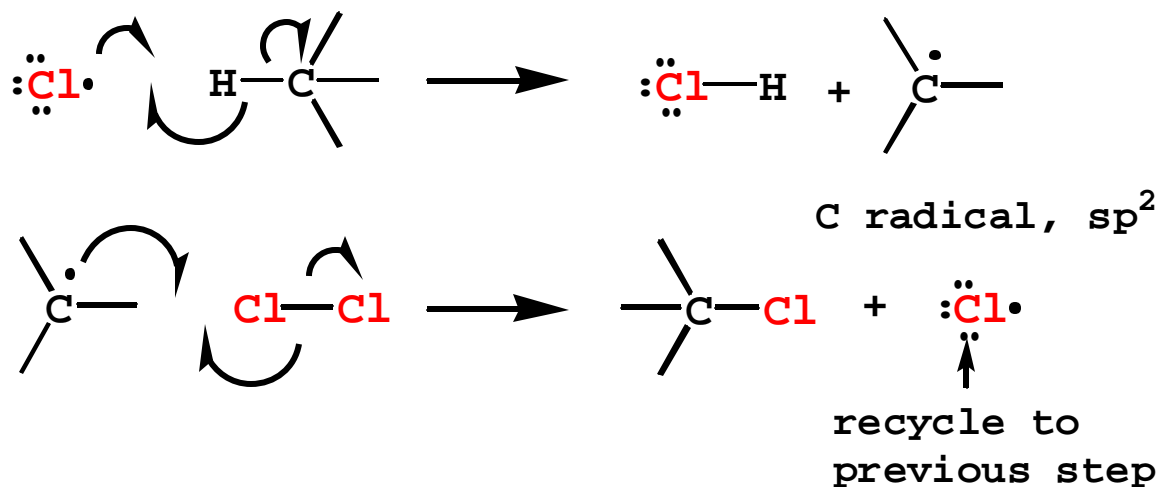
Step # 1 = **initiation step** (form halogen atoms)

weakest bond breaks first

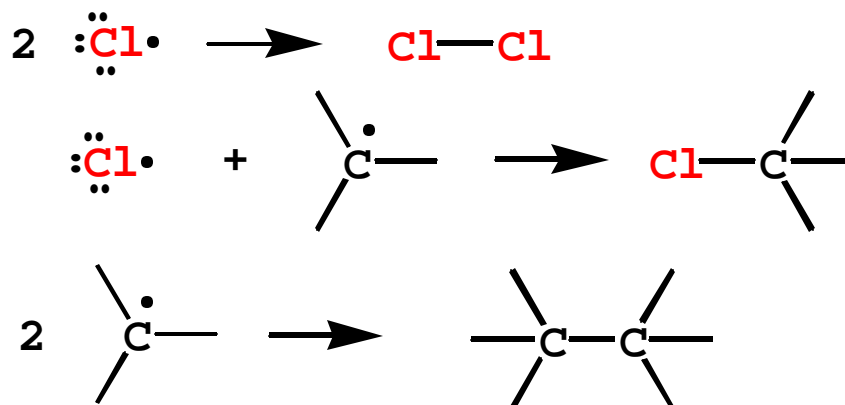
Bond	Bond Energy
Cl-Cl	243 kJ/mol
C(sp ³)-H	438
C(sp ²)-H	464
C(sp ³)-C(sp ³)	376



Step # 2 = **two propagation steps**
(form C radicals)



Step # 3 = **three chain termination steps** (remove
components necessary for propagation)



As a result of combining two C radicals, the chlorination of methane yields a small amount of ethane.

Question: What are the products of bromination of ethane?

Regioselectivity of bromination is substantially greater than chlorination.

Relative rates of R-H substitution...

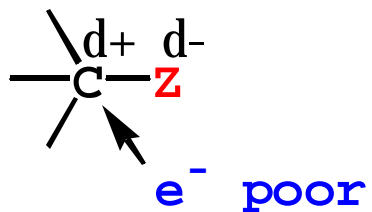
X = Cl or Br	R ₃ CH	R ₂ CH ₂	RCH ₃
chlorination	5.2	3.9	1
bromination	1640	82	1

http://www.chem.umd.edu/courses/chem233/ReactionMechanisms/radicals/Free_radical_halogenation.htm

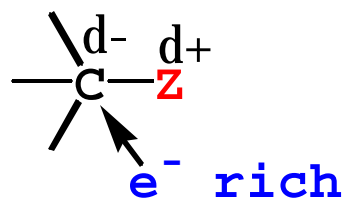
For more information on radical structure and stability, see:

<http://www.chem.umd.edu/courses/chem233/ReactionMechanisms/radicals/Cradicalstructuresandstabilities-html.htm>

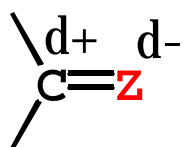
*Bond polarity (examples in Table 5.1)...



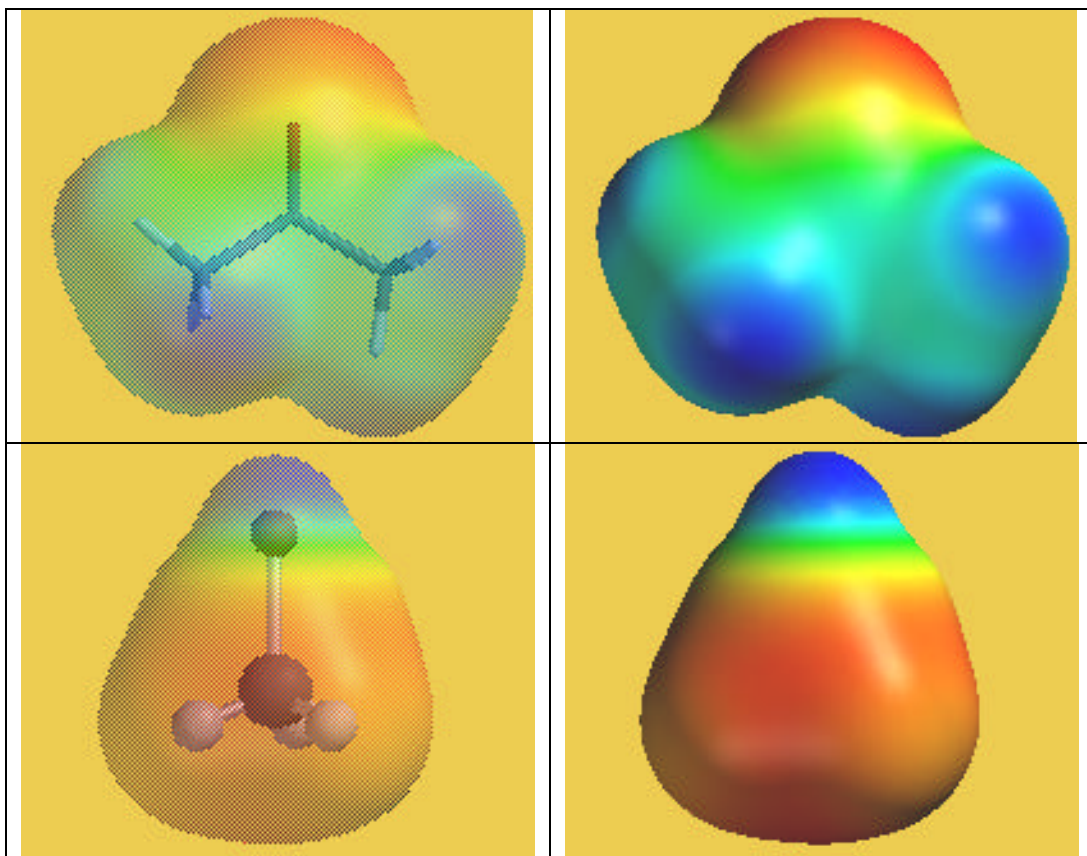
Z = O, N, halogens



Z = MgX, Li

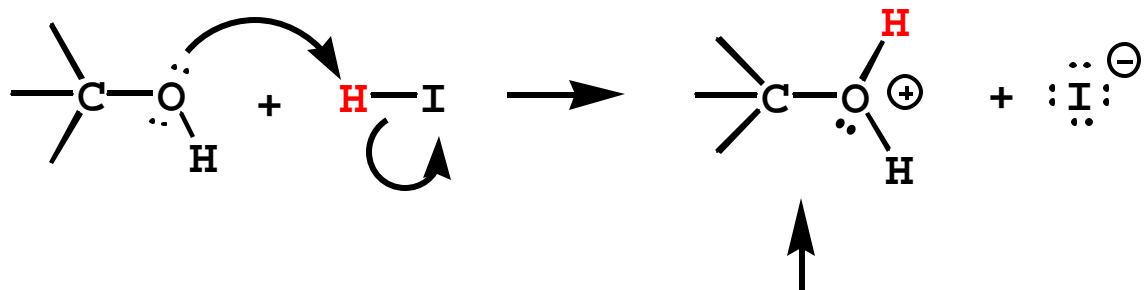


Z = O, S, N



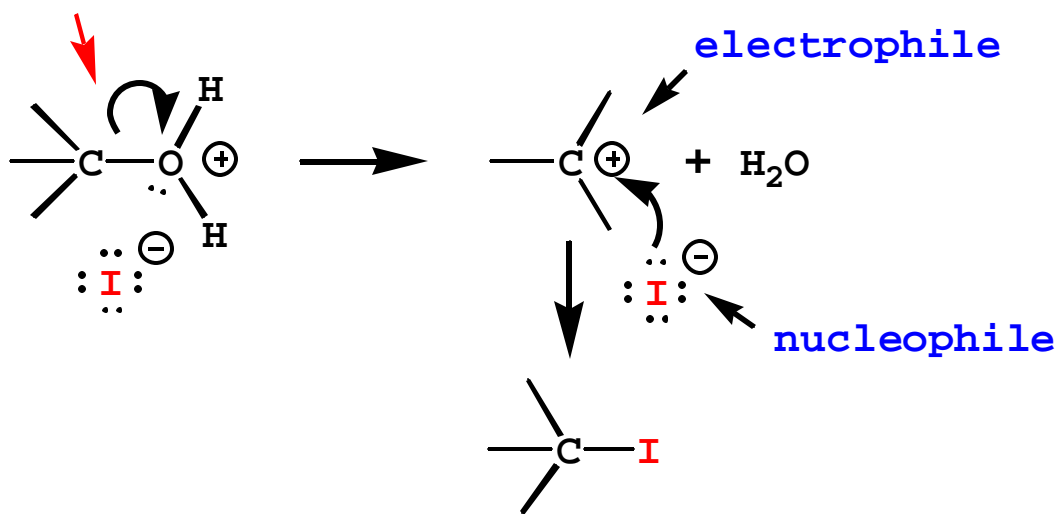
*Polar reactions...

Example # 1...alcohol + HI...

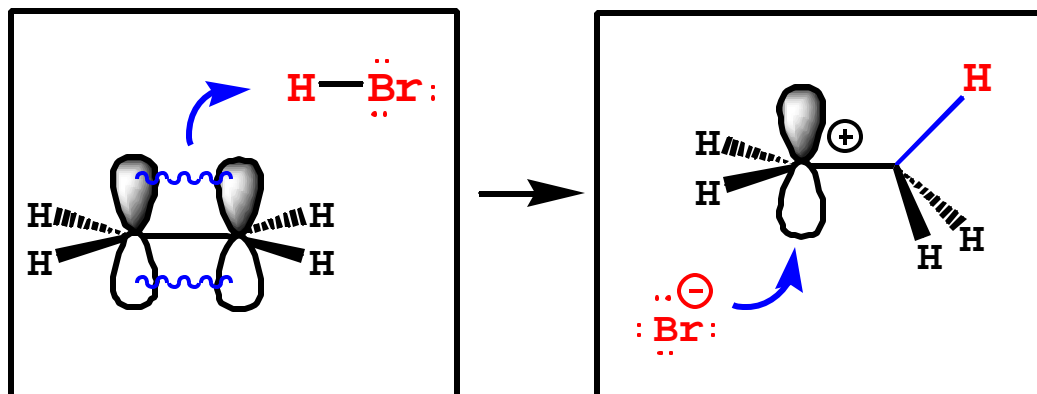
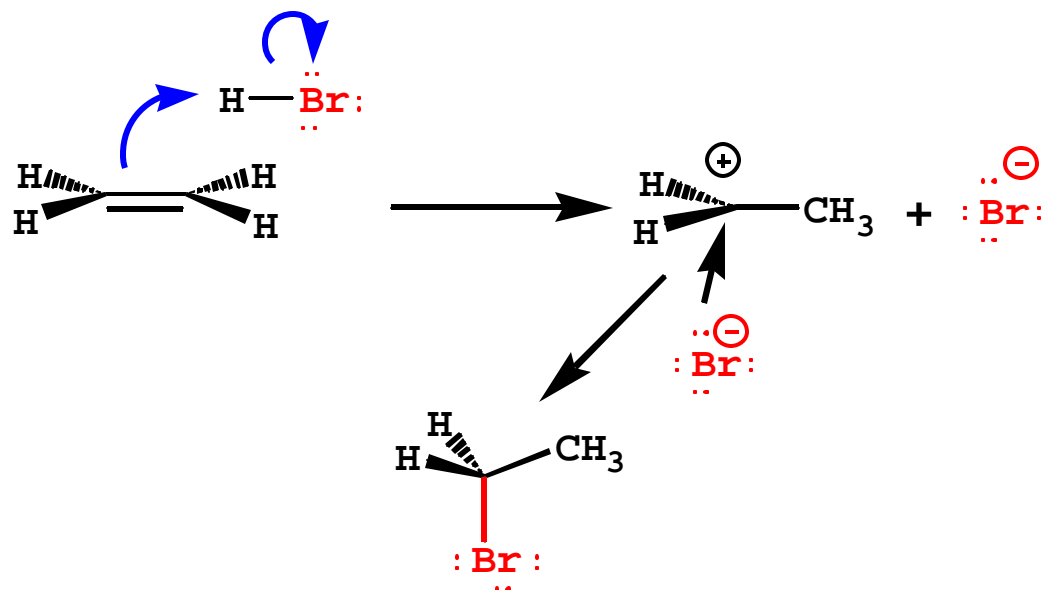


oxonium cation; C-O bond is polarized

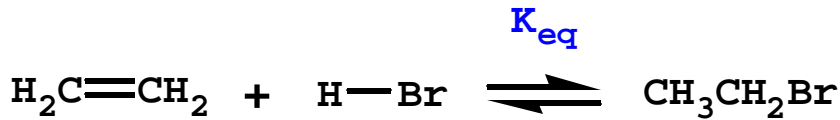
C-O breaks
heterolytically



Example # 2...alkene + HBr...




*Rates & equilibria...



$$K_{\text{eq}} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{H}_2\text{C}=\text{CH}_2][\text{HBr}]} = 7.5 \times 10^7$$

$$\text{DG}^\circ = -RT \ln K_{\text{eq}} \quad (\text{R} = 8.314 \text{ J/mol}\cdot\text{K})$$

 Gibbs free energy change

$$\text{DG}^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$$

$$\text{DG}^\circ < 0, K_{\text{eq}} > 1$$

$$\text{DG}^\circ = 0, K_{\text{eq}} = 1$$

$$\text{DG}^\circ > 0, K_{\text{eq}} < 1$$

Basic equation: $\text{DG}^\circ = \text{DH}^\circ - \text{TDS}^\circ$

For the above reaction at $T = 298 \text{ K}$...

$$\text{DG}^\circ = -44.8 \text{ kJ/mol} = -RT \ln(7.5 \times 10^7)$$

$$\text{DH}^\circ = -84.1 \text{ kJ/mol}$$

$$\text{DS}^\circ = -0.132 \text{ kJ/mol}\cdot\text{K} \quad (\text{TDS}^\circ = 39.3 \text{ kJ/mol})$$

Few other examples...



$$\Delta H^\circ = +93.7 \text{ kJ/mol}$$

$$\Delta S^\circ = +0.14 \text{ kJ/mol}\cdot\text{K}$$



$$\Delta H^\circ = -64.9 \text{ kJ/mol}$$

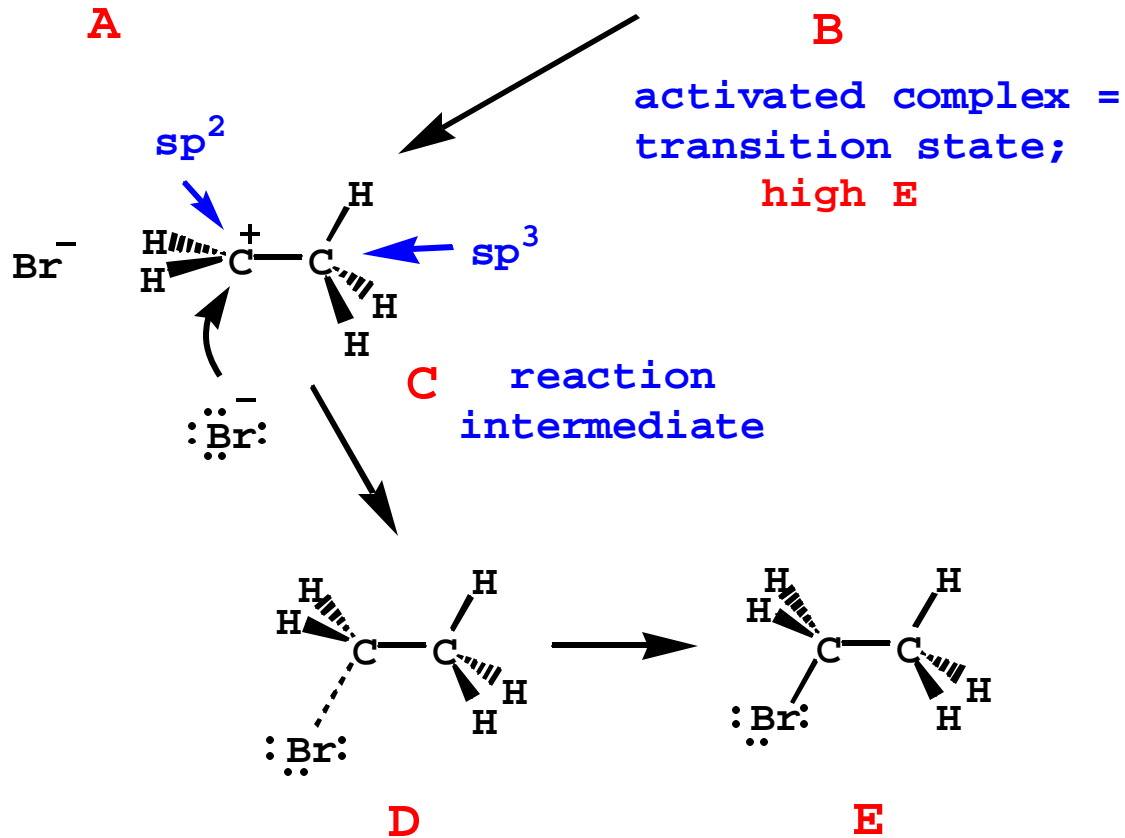
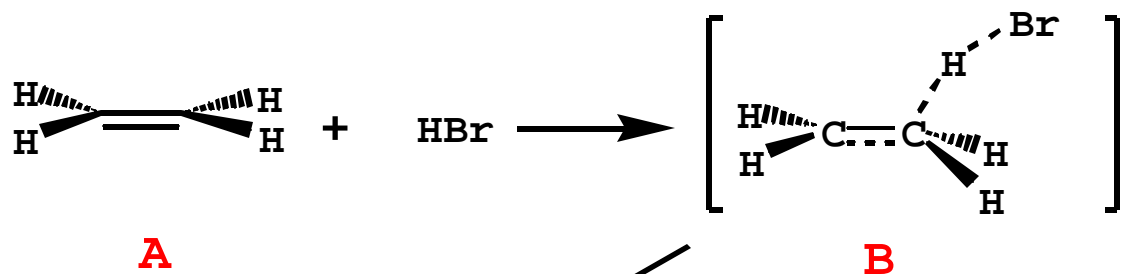
$$\Delta S^\circ = -0.131 \text{ kJ/mol}\cdot\text{K}$$

Calculated ΔH° from bond energies...

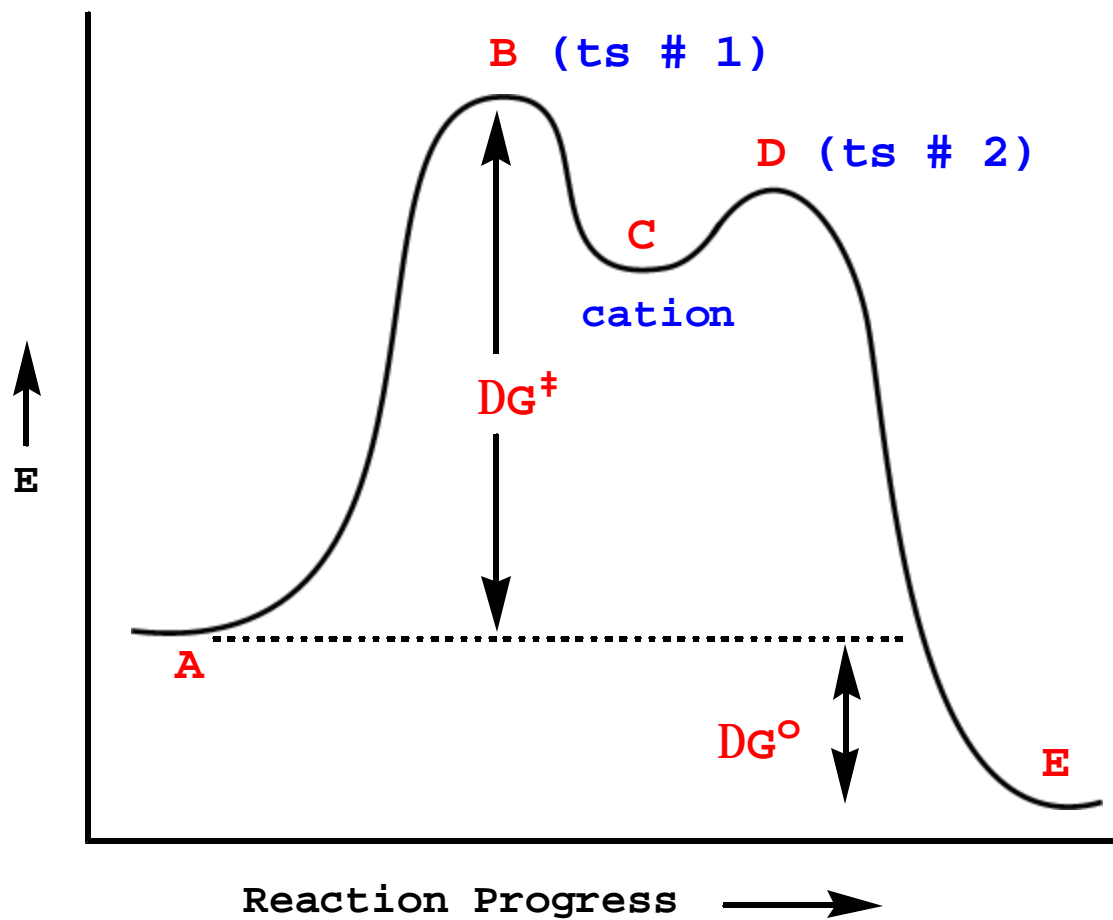
break C-C π -bond	+ 235 kJ/mol
break H-Cl bond	+ 432
form C-Cl bond	- 338
form C-H bond	- 420

$$\Delta H^\circ = -91.0 \text{ kJ/mol}$$

*Consider the following reaction..

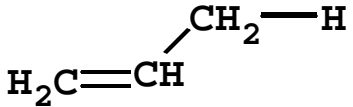
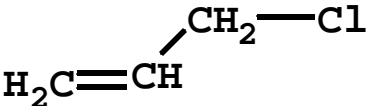
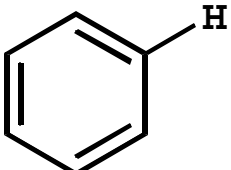
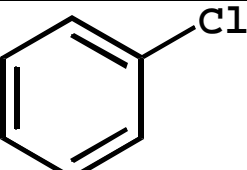
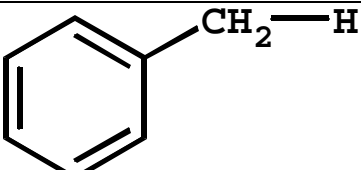
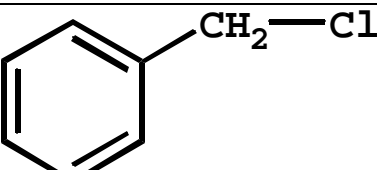
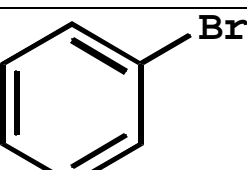
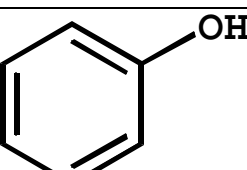


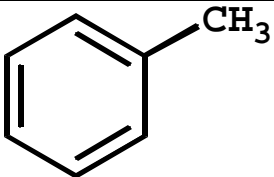
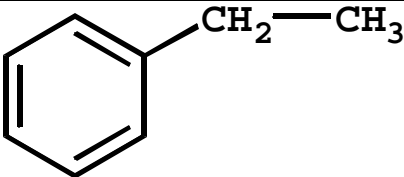
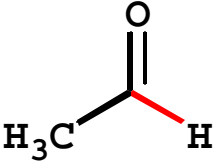
Potential E diagram for the reaction...

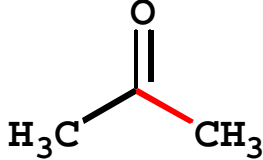
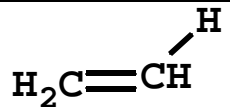
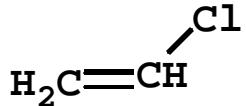


For this reaction, exptl $DG^\ddagger = 140$ kJ/mol;
 DG^\ddagger for most organic reactions is 40-140 kJ/mol;
reaction occurs at or below RT if $\Delta G^\ddagger = 80$ kJ/mol

Bond Dissociation Energies (Table 5.3)

Bond	E kJ/mol	Bond	E kJ/mol
H—H	436		361
H—F	570		289
H—Cl	432		464
H—Br	366		405
H—I	298		368
Cl—Cl	243		293
Br—Br	193		337
I—I	151		469

$\text{H}_3\text{C}-\text{H}$	438	$\text{HC}\equiv\text{C}-\text{H}$	552
$\text{H}_3\text{C}-\text{Cl}$	351	$\text{H}_3\text{C}-\text{CH}_3$	376
$\text{H}_3\text{C}-\text{Br}$	293	$\text{C}_2\text{H}_5-\text{CH}_3$	355
$\text{H}_3\text{C}-\text{I}$	234	$(\text{H}_3\text{C})_2\text{HC}-\text{CH}_3$	351
$\text{H}_3\text{C}-\text{OH}$	380	$(\text{H}_3\text{C})_3\text{C}-\text{CH}_3$	339
$\text{H}_3\text{C}-\text{NH}_2$	335	$\text{H}_2\text{C}=\text{CH}-\text{CH}_3$	406
$\text{C}_2\text{H}_5-\text{H}$	420	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$	310
$\text{C}_2\text{H}_5-\text{Cl}$	338	$\text{H}_2\text{C}=\text{CH}_2$	611
$\text{C}_2\text{H}_5-\text{Br}$	285		427
$\text{C}_2\text{H}_5-\text{I}$	222		332
$\text{C}_2\text{H}_5-\text{OH}$	380		368
$(\text{H}_3\text{C})_2\text{HC}-\text{H}$	401	$\text{HO}-\text{H}$	498
$(\text{H}_3\text{C})_2\text{HC}-\text{Cl}$	339	$\text{HO}-\text{OH}$	213
$(\text{H}_3\text{C})_2\text{HC}-\text{Br}$	274	$\text{H}_3\text{CO}-\text{H}$	437
$(\text{H}_3\text{C})_3\text{C}-\text{H}$	390	$\text{H}_3\text{CS}-\text{H}$	371
$(\text{H}_3\text{C})_3\text{C}-\text{Cl}$	330	$\text{C}_2\text{H}_5\text{O}-\text{H}$	436

$(\text{H}_3\text{C})_3\text{C}-\text{Br}$	263		322
$(\text{H}_3\text{C})_3\text{C}-\text{I}$	209	$\text{C}_2\text{H}_5\text{O}-\text{CH}_3$	339
	444	$\text{H}_2\text{N}-\text{H}$	449
	368	$\text{H}-\text{CN}$	518

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