

Notes: 3-8

Thursday, March 08, 2007
5:35 PM

Last Time: Optical Activity Free Radical Chain Reactions

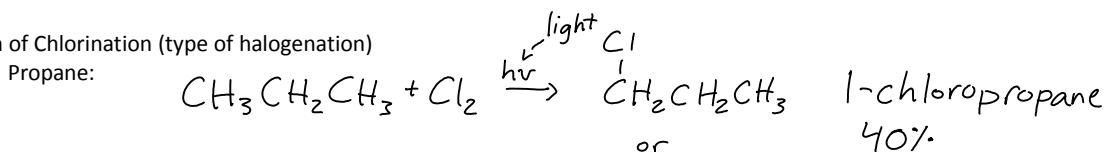
Today: Chlorination vs Bromination Allylic Bromination

Ethane: CH_3CH_3

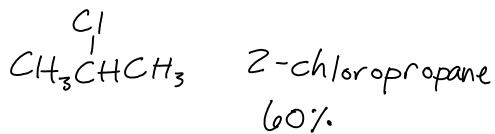
Propane:

1° = primary 2° secondary

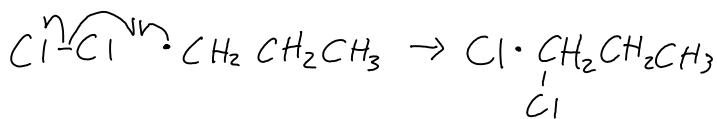
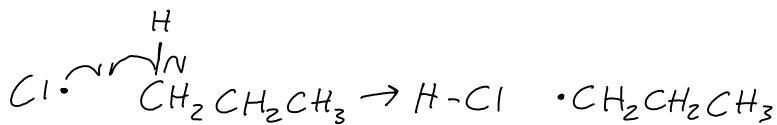
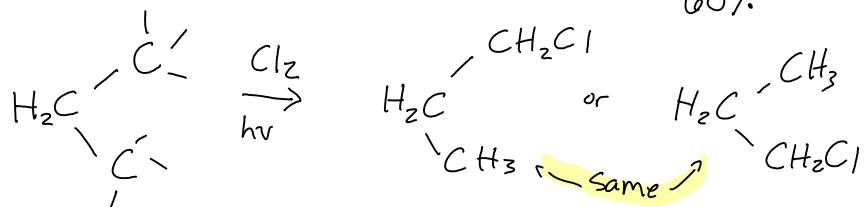
Mechanism of Chlorination (type of halogenation)

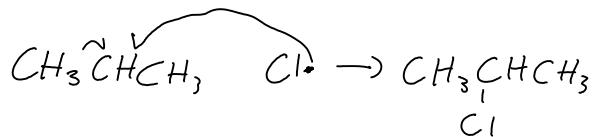
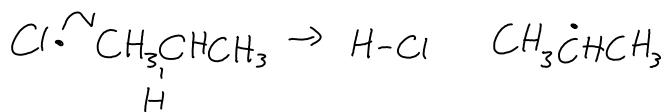
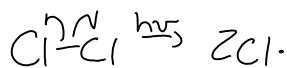


Replacement of hydrogen is specific - not random



Mechanism:





$3^\circ > 2^\circ > 1^\circ$ - stability of free radicals

How reactive are the hydrogens?

$$\frac{40\%}{6 \text{ } 1^\circ\text{H}} = 6.67 \text{ per H}$$

$$\frac{60\%}{2 \text{ } 2^\circ\text{H}} = 30\% \text{ per H}$$

Compare the 2° H reactivity to 1° reactivity

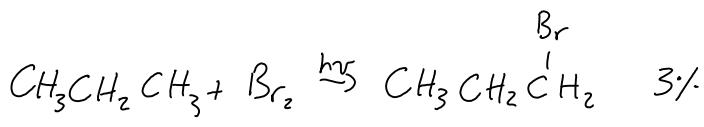
$30: 6.67$

$2^\circ: 1^\circ$

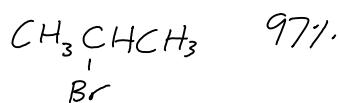
$4.5: 1$

2° Hs are 4.5x as reactive as 1° Hs

Bromination is more selective than Chlorination.



or



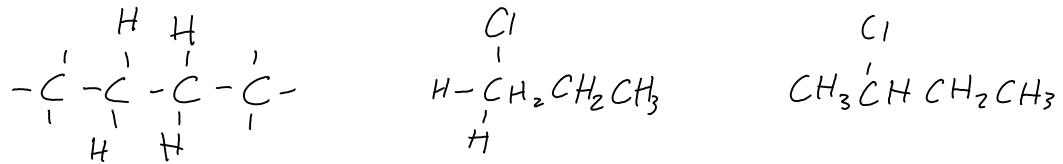
$$\frac{3\%}{6 \text{ } 1^\circ\text{H}} = .5\%$$

$$\frac{48.5}{.5} = 97\%$$

$$\frac{97\%}{2 \text{ } 2^\circ\text{H}} = 48.5\%$$

2°H are 97 times reactive as 1°H

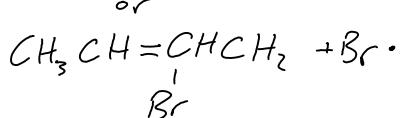
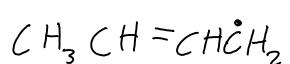
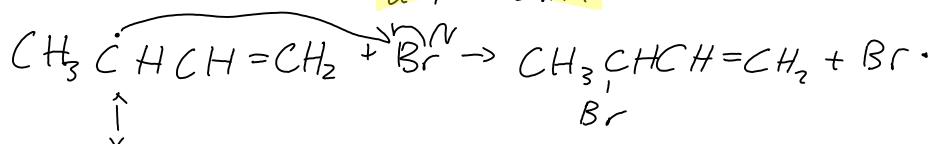
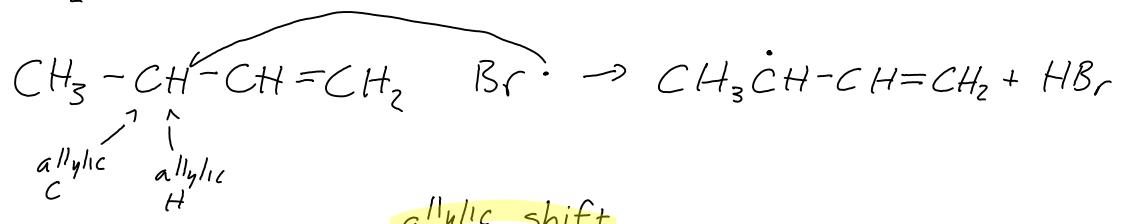
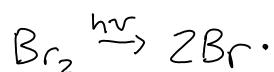
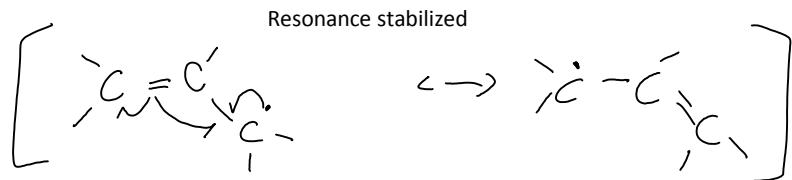
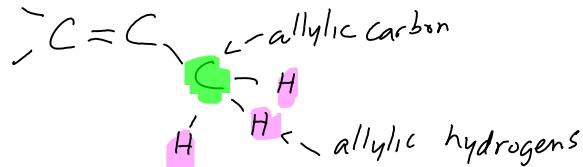
Florine is not selective at all... is approx 50% between 2^0 and 1^0



To control for multiple halogenations: use small amount of halogen and excess alkane

Allylic Free Radicals:

Free Radical Bromination and allylic shift



Free radical stabilization: allylic > 3^0 > 2^0 > 1^0 > vinylic