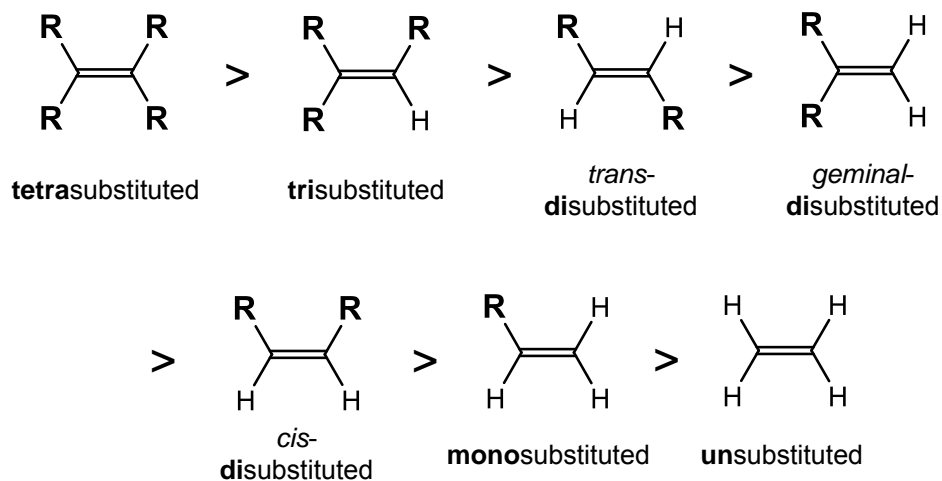


# Relative Stability of Alkenes

- More substituted alkenes are more stable.
- Having sterically demanding substituents on opposite sides of an alkene is better than on the same side.

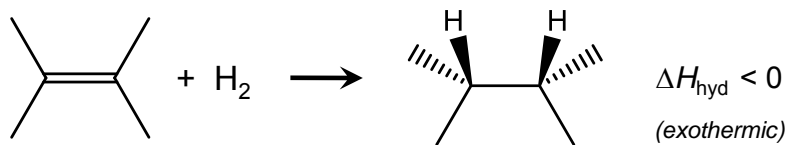
Stability:



# Molar Heats of Hydrogenation of Alkenes

Originally, differences in alkene stability were discovered via differences in their hydrogenation enthalpy.

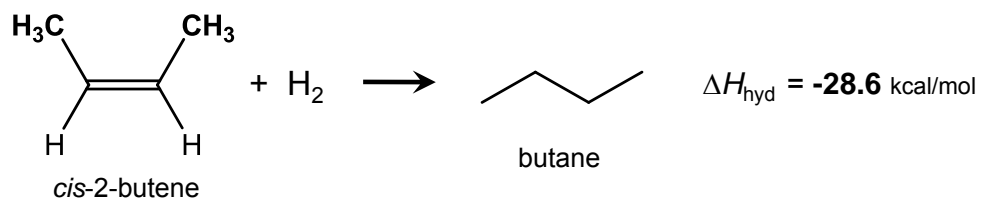
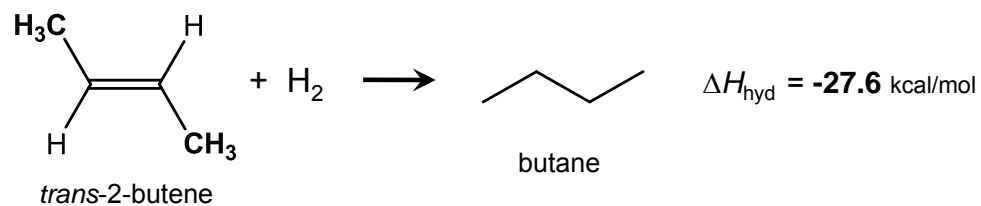
*Hydrogenation:*



Don't worry about mechanism, etc.

Just using this reaction to think about alkenes.

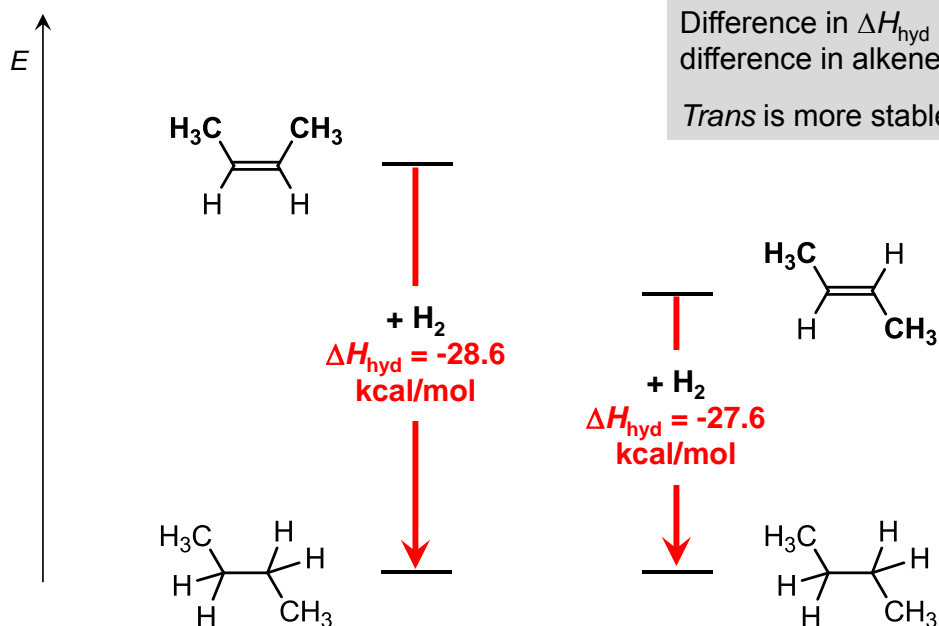
## Molar Heats of Hydrogenation of Alkenes



Question: These two reactions both convert  $\text{C}_4\text{H}_8$  to the same product. But they have different reaction energies. Why?

Answer: Difference in  $\Delta H_{\text{hyd}}$  reflects difference in alkene stability.

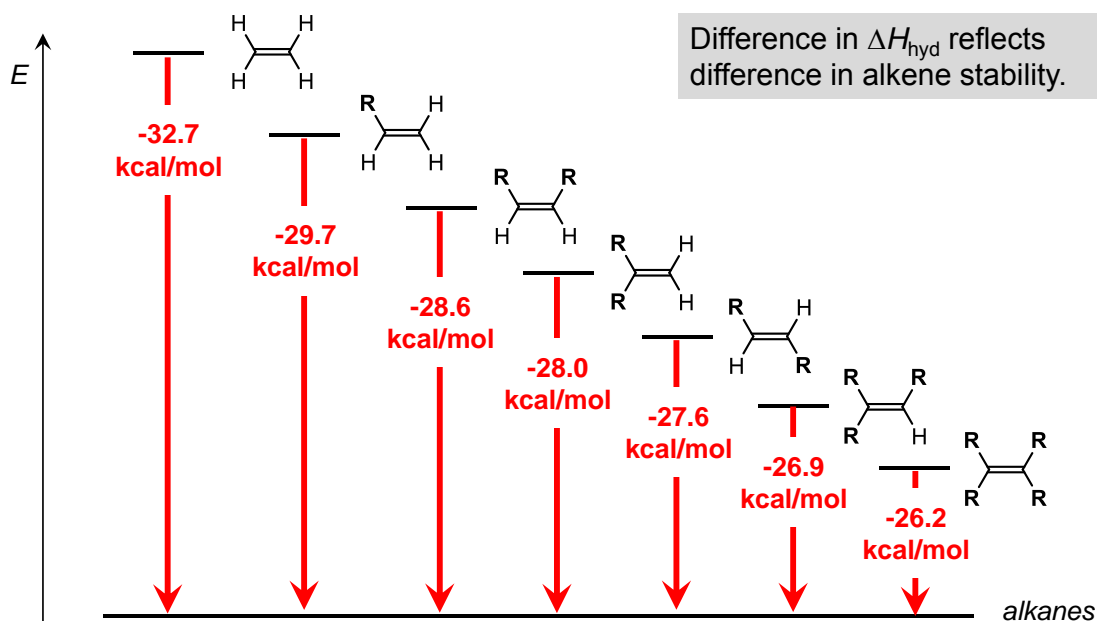
## Relative Stability of Alkenes, Based On Molar Heats of Hydrogenation



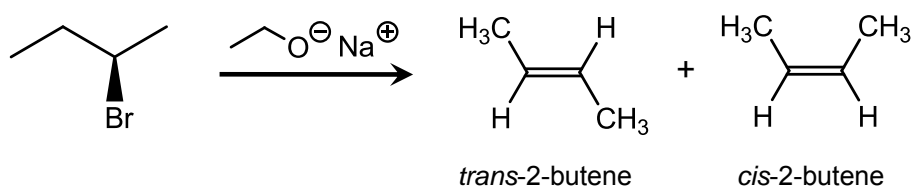
Difference in  $\Delta H_{\text{hyd}}$  reflects difference in alkene stability.

*Trans* is more stable than *cis*.

## Relative Stability of Alkenes, Based On Molar Heats of Hydrogenation

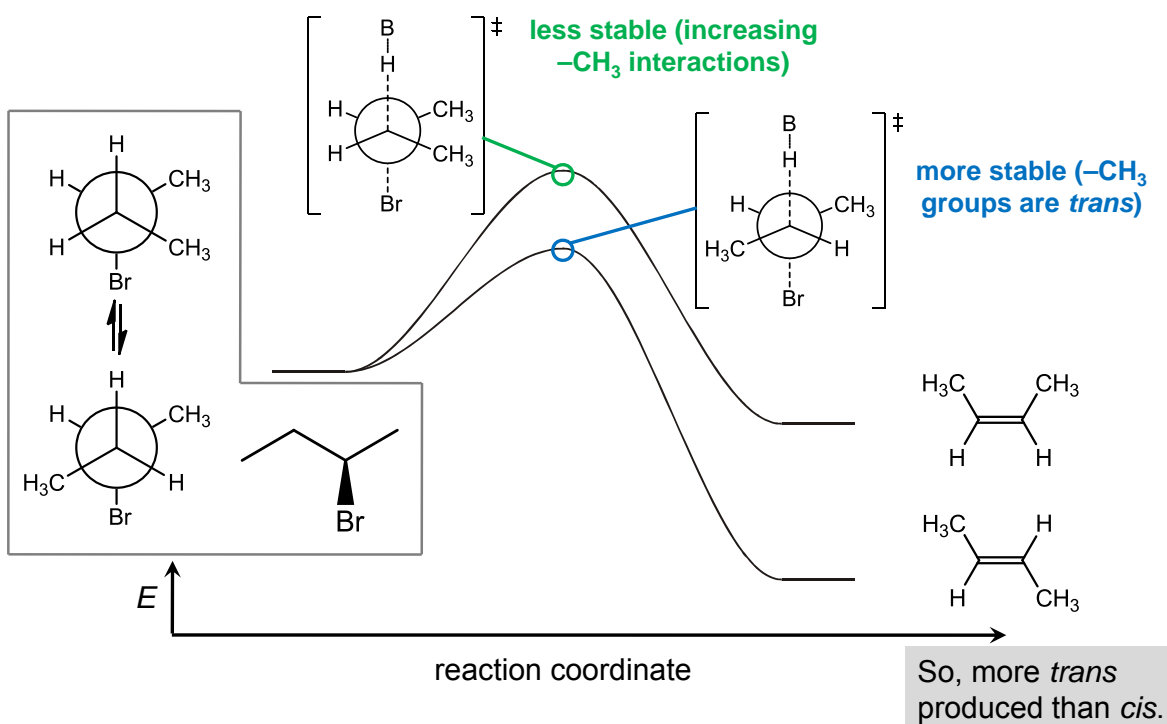


## Elimination Reactions Typically Produce the Most Stable Alkene Product



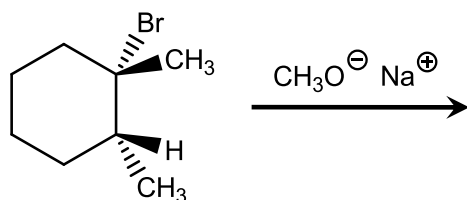
Which product would predominate? Why?

## Elimination Reactions Typically Produce the Most Stable Alkene Product



## Zaitsev's Rule: Elimination Reactions Produce the Most Substituted Alkene

In-Class Exercise:

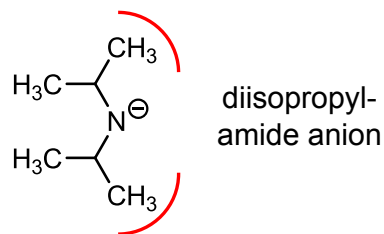
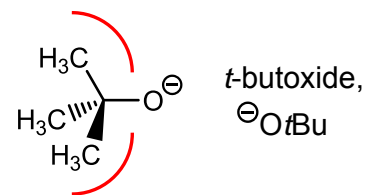
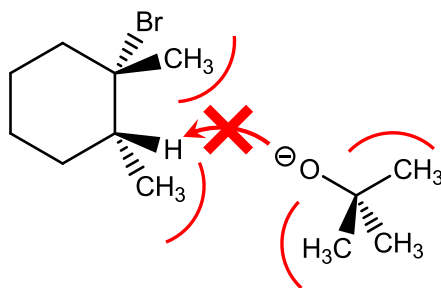


What three products would be generated?  
Which would be favored?

## Exception to Zaitsev's Rule: Sterically Hindered Bases

If the electron-donating atom in the eliminating base is sterically hindered, the base cannot access 3° or 2° protons as easily.

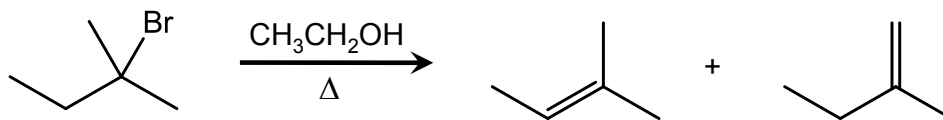
*Example:*



*Result:* Elimination here favors least substituted alkene. (Sometimes called "Hofmann selectivity".)

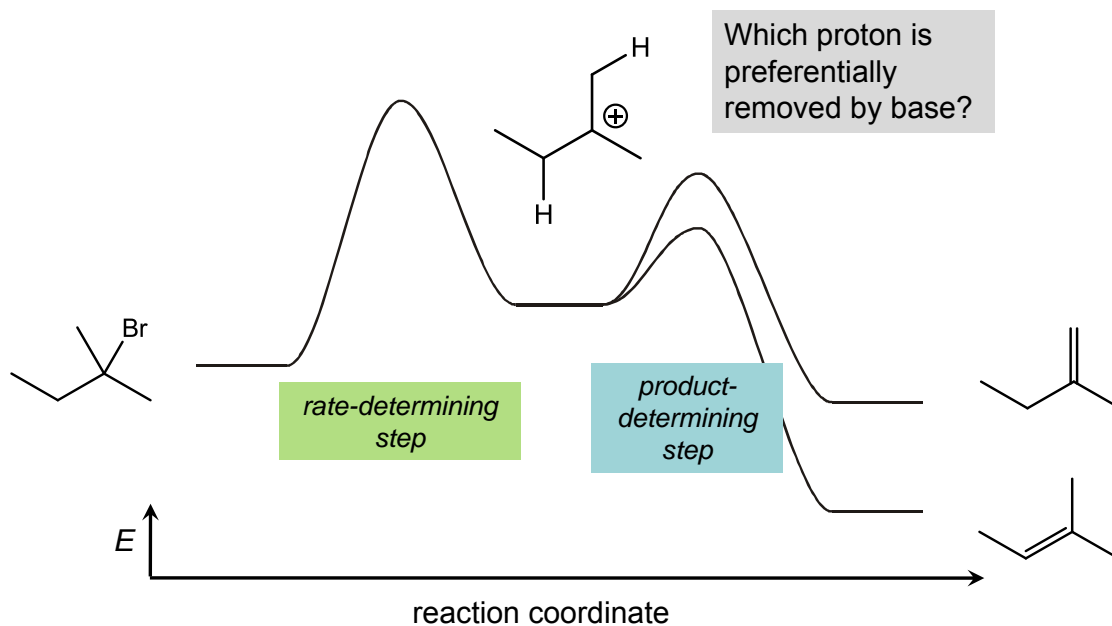
## E1 Also Produces the Most Stable, Most Substituted Alkene Product

(Zaitsev's Rule also applies to E1.)



Which product would predominate? Why?

## E1 Also Produces the Most Most Stable, Substituted Alkene Product



## Predicting Reaction Patterns

### $S_N2$

- Unhindered  $1^\circ$  halides as substrates ( $2^\circ$  ok)
- Better nucleophiles than bases:  
 $I^-$ ,  $Br^-$ ,  $CH_3CO_2^-$ ,  $RS^-$ ,  $HS^-$ ,  
 $CN^-$ ,  $N_3^-$

### E2

- $2^\circ$  or  $3^\circ$  halide as substrate
- Better bases than nucleophiles:  
 $HO^-$ ,  $RO^-$ , (esp.  $tBuO^-$ ),  
 $RC\equiv C^-$ ,  $R_3N$ ,  $H_3N$
- Preferred over  $S_N2$  when product alkene is highly substituted

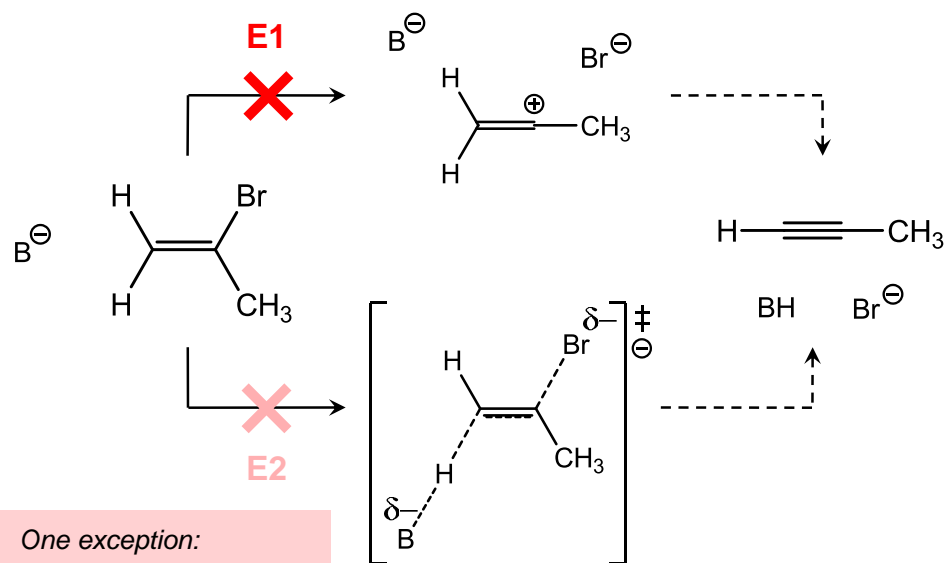
### $S_N1$

- $2^\circ$  or  $3^\circ$  halide as substrate
- Neutral or acidic conditions,  $\Delta$
- Better nucleophiles than bases:  
 $RSH$ ,  $H_2S$ ,  $CH_3COOH$

### E1

- $2^\circ$  or  $3^\circ$  halide as substrate
- Neutral or acidic conditions,  $\Delta$
- Better bases than nucleophiles:  
 $H_2O$ ,  $ROH$
- Preferred over  $S_N1$  when product alkene is highly substituted

# E1 and E2 at $sp^3$ -Hybridized Carbon Only



One exception:

