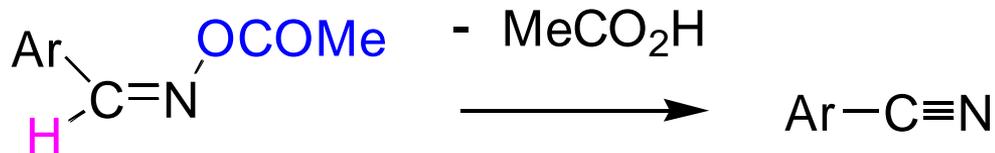
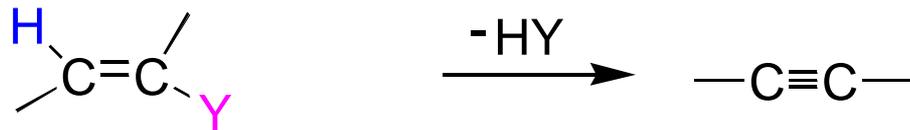
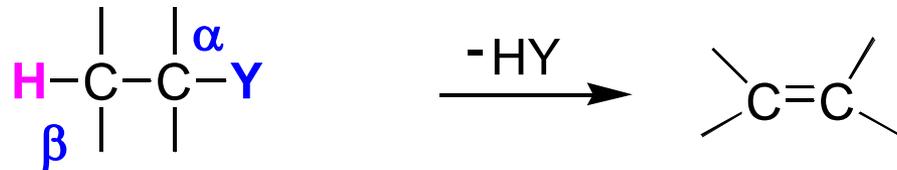
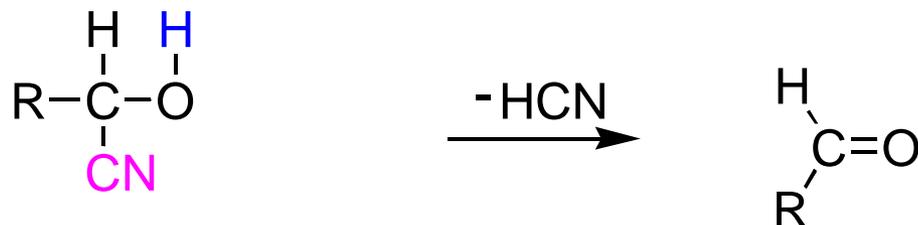


REAÇÕES DE ELIMINAÇÃO

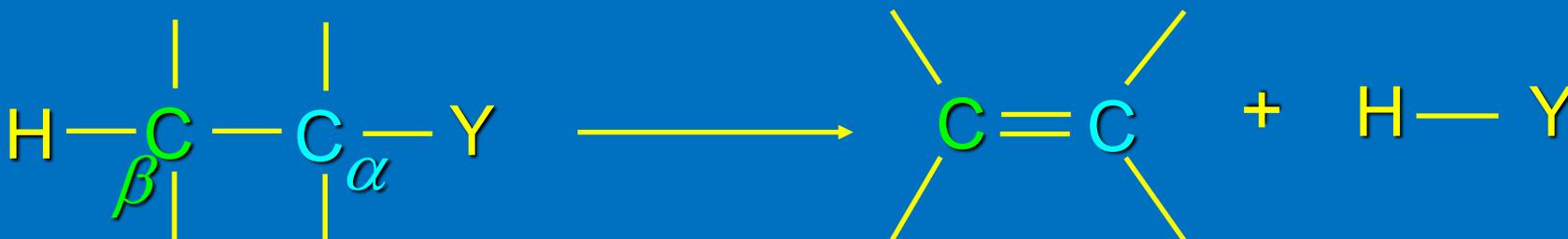


Eliminação β
Eliminação 1,2



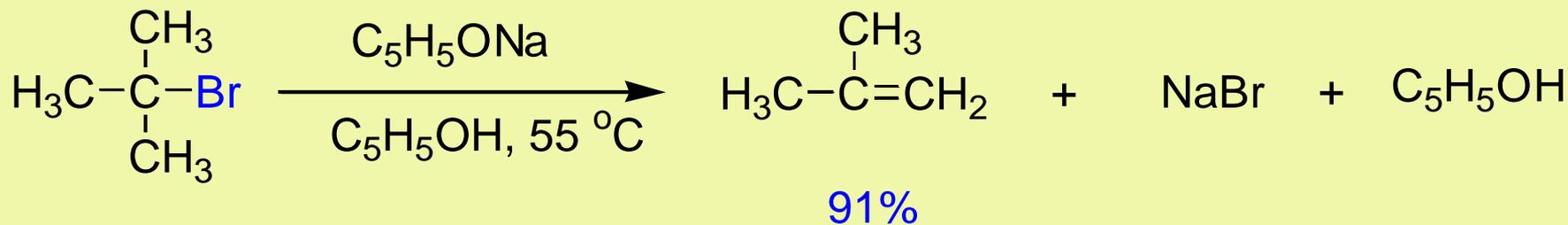
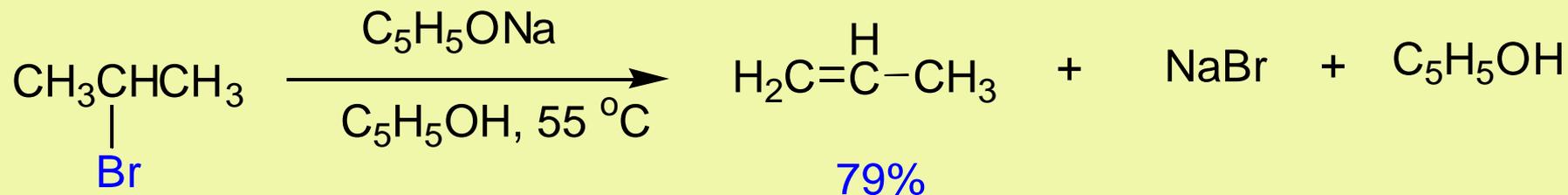
Reações de β -Eliminação

- Desidrogenação de alcanos:
processo industrial; não regioseletivo
- Desidratação de álcoois:
catalisada por ácido
- Desidro-halogenação de haletos de alquila:
consome base



Desidro-halogenação de haletos de alquila

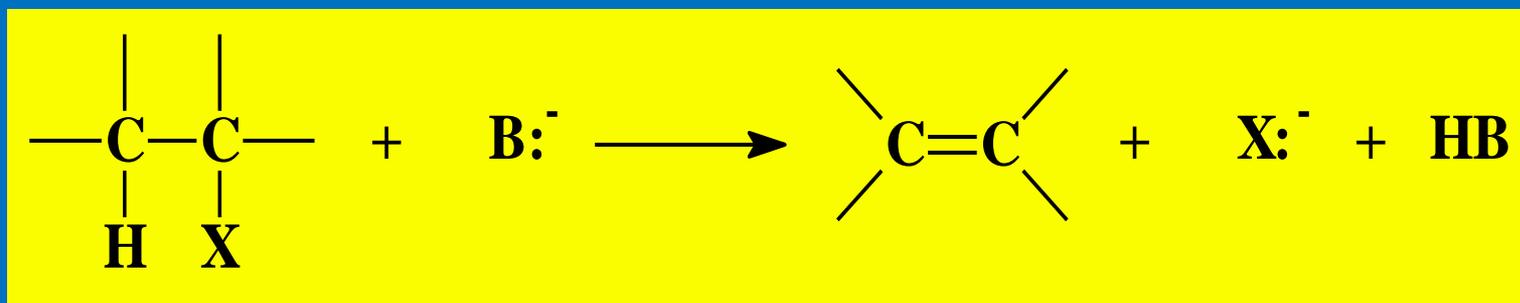
Aquecimento do R-X em presença de bases fortes leva ao alceno



Reações de Eliminação

Exemplo: Obtenção de alcenos

(desidro-halogenação  -HX)



- Perda de halogênio como íon haleto
- Perda de H⁺ do carbono adjacente, para uma base
- Formação de uma ligação pi.

Possível mecanismo para a
desidro-halogenação de haletos de alquila:
o mecanismo E2

Fatos

- (1) a desidro-halogenação de haletos de alquila exhibe cinética de segunda-ordem
1ª ordem, para o haleto de alquila
1ª ordem, para a base

$$\text{velocidade} = k[\text{haleto de alquila}][\text{base}]$$

implica em que tanto a base como o haleto de alquila estejam envolvidos no passo que determina a velocidade de reação; *i.e.*, ele é bimolecular (segunda ordem)

Fatos

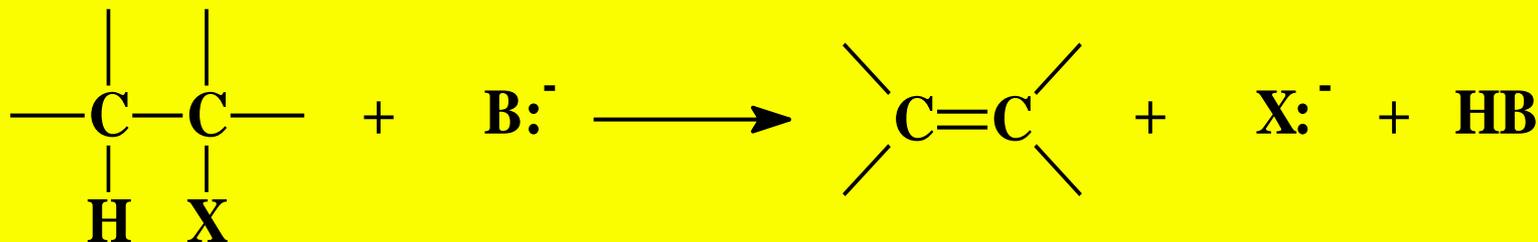
- (2) velocidade de eliminação é dependente do halogênio

ligações C—X mais fracas: velocidades maiores

velocidade: $RI > RBr > RCl > RF$

implica em que haja quebra da ligação carbono-halogênio no passo determinante da velocidade de reação

Mecanismo E2



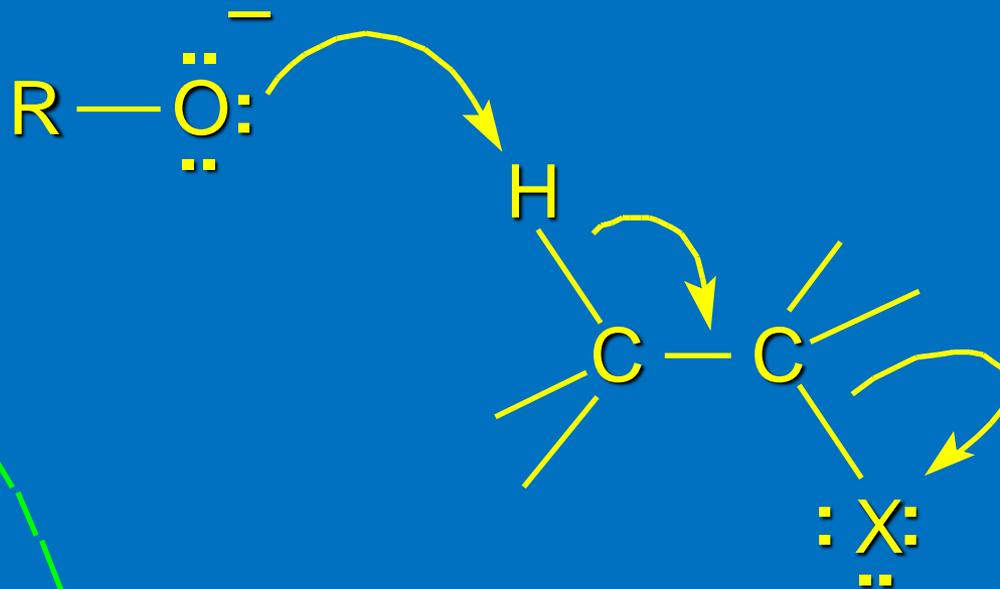
- processo bimolecular concertado (um passo)
- estado de transição único

Quebra da ligação C—H

Formação do componente π da ligação dupla

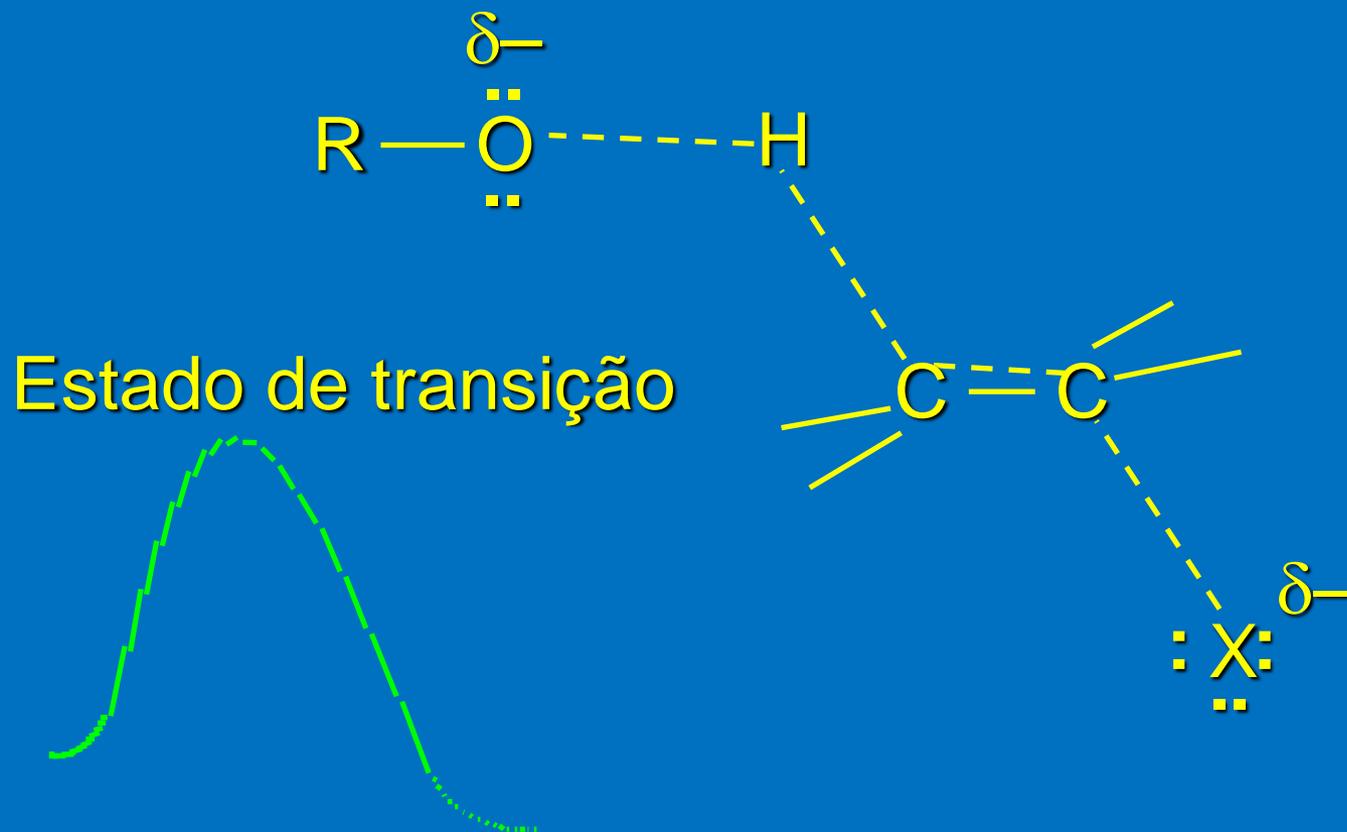
Quebra da ligação C—X

Mecanismo E2

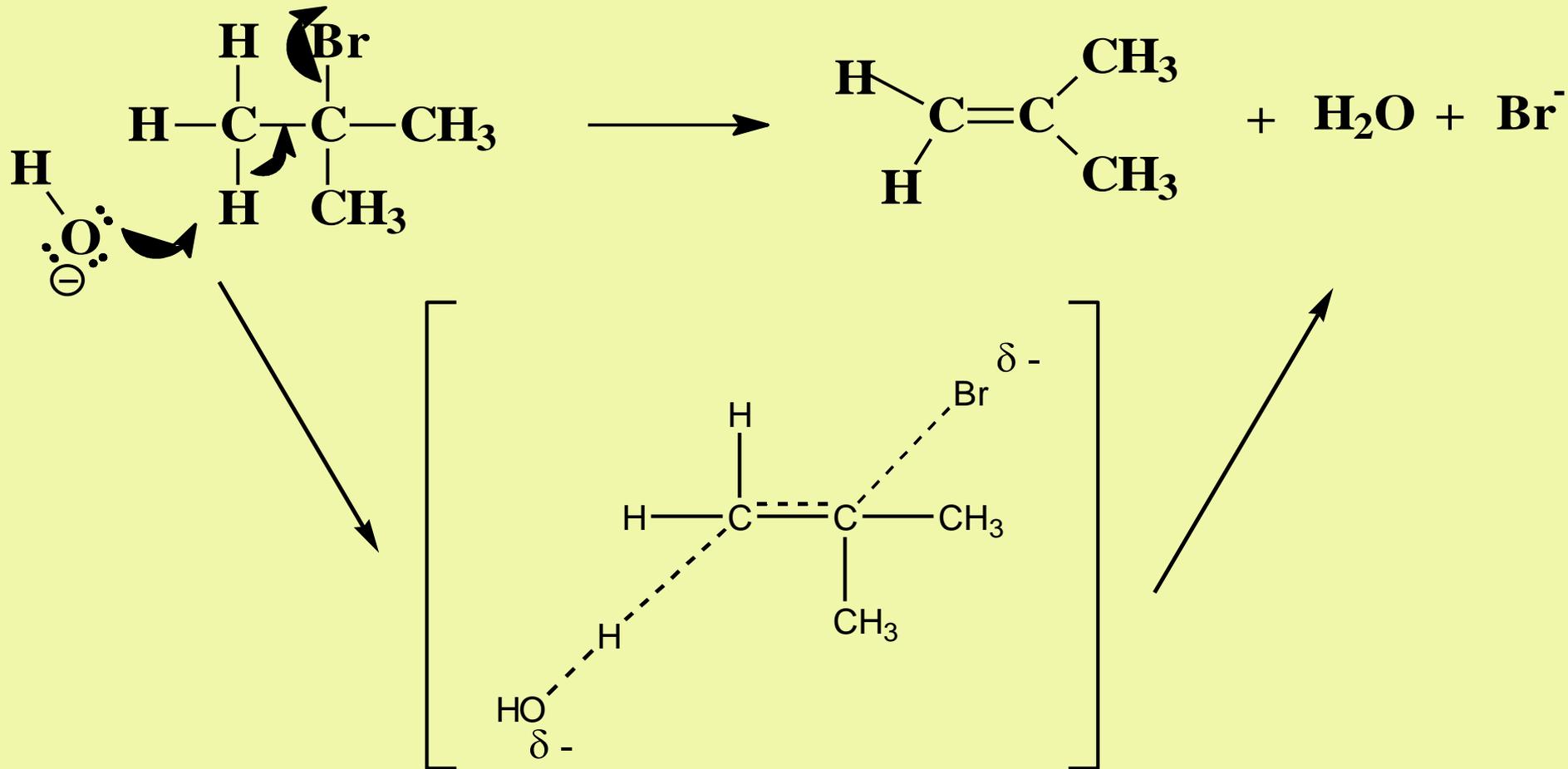


Reagentes

Mecanismo E2



Mecanismo E2: eliminação bimolecular

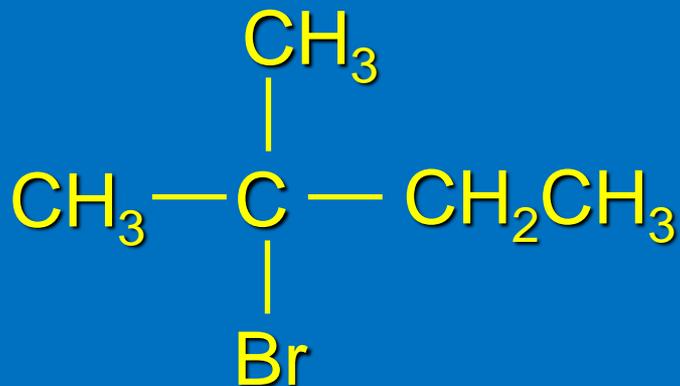


◆ **Requer uma base forte**

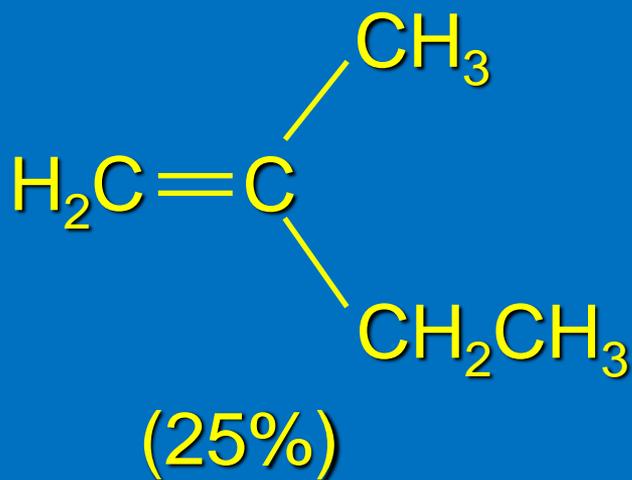
◆ **Saída do haleto e abstração de próton acontecem concertadamente – não há intermediários**

Outra possibilidade para o mecanismo
das eliminações em haletos de alquila:
o mecanismo E1

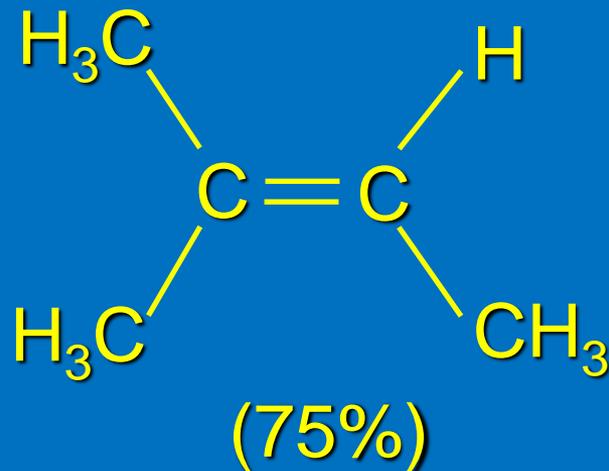
Exemplo



Etanol, aquecimento



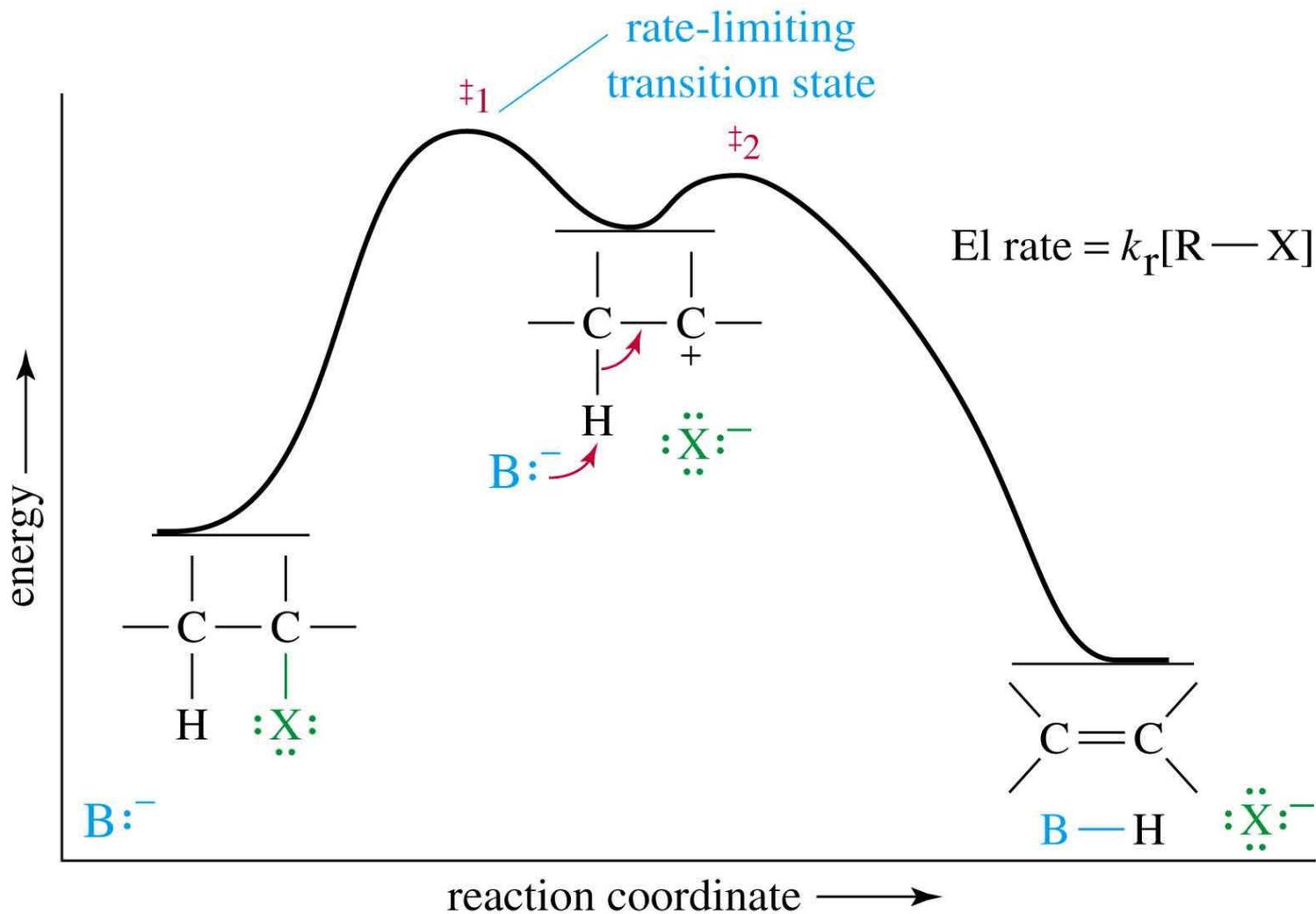
+



Mecanismo E1

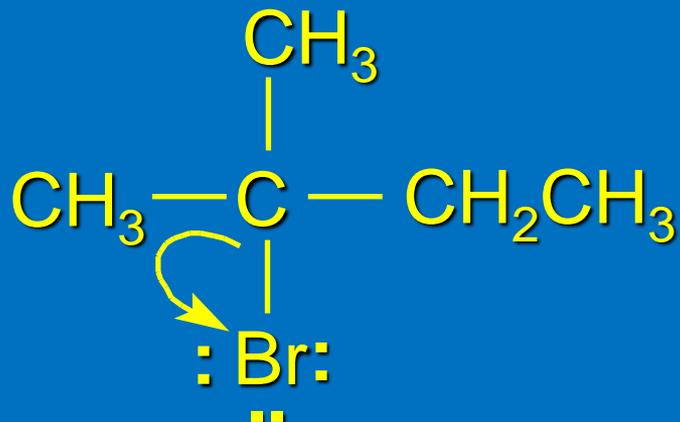
1. Ocorrem eliminações em haletos de alquila, mesmo na ausência de bases.
2. Carbocátions são intermediários.
3. O passo determinante da velocidade é a ionização unimolecular do haleto de alquila.
4. Para haletos terciários, em geral a base é fraca e em baixas concentrações.

Diagrama de Energia: E1

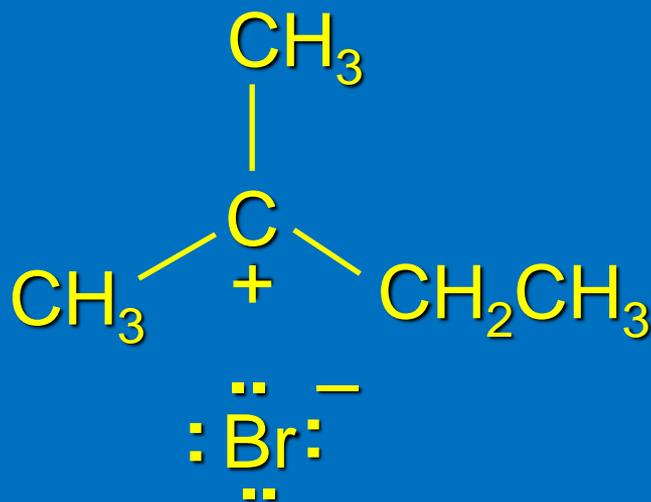


◆ Nota: primeiro passo é igual ao proposto para as S_N1

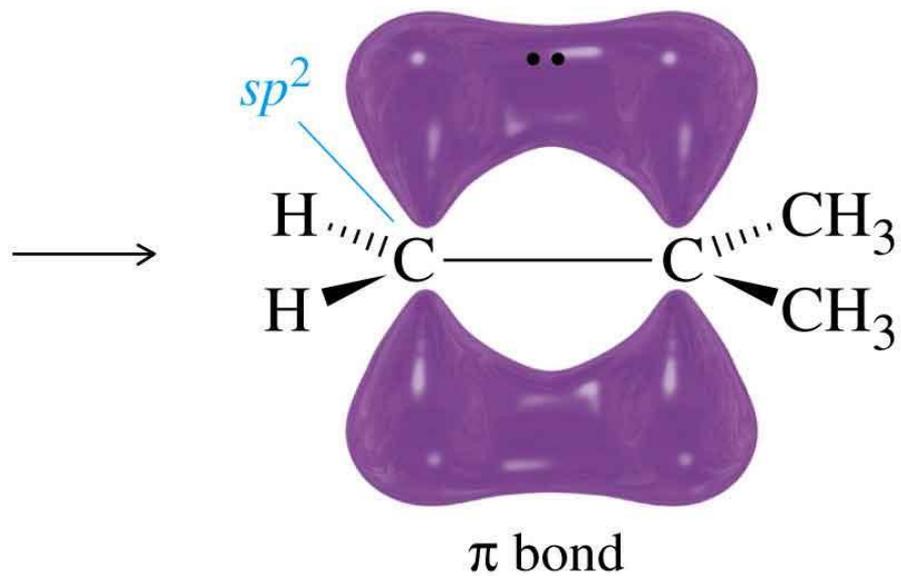
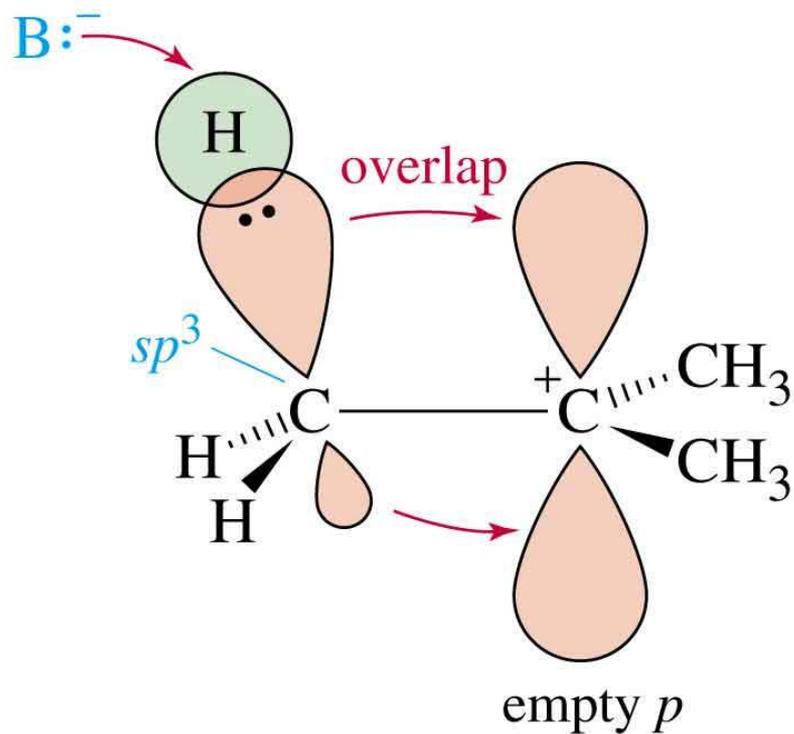
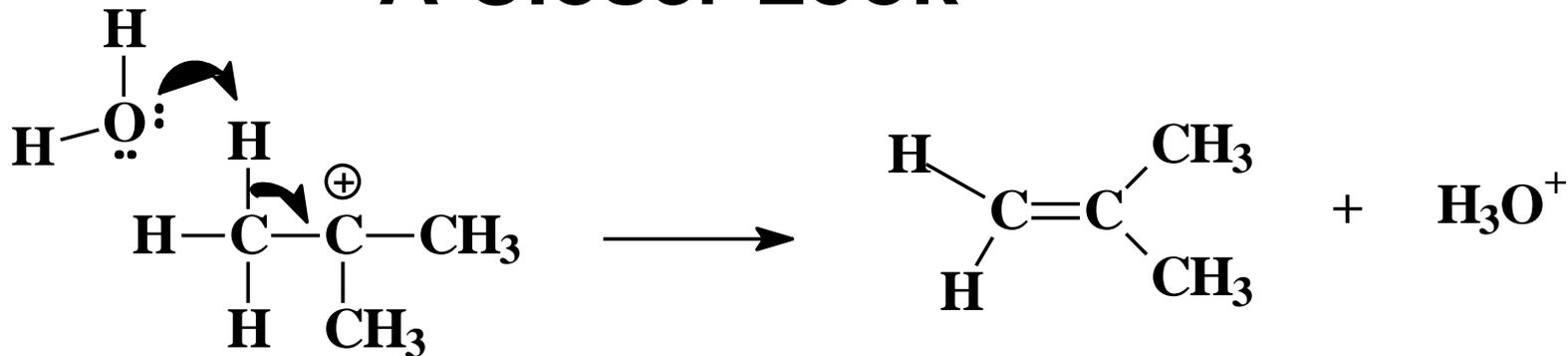
Passo 1



lento, unimolecular



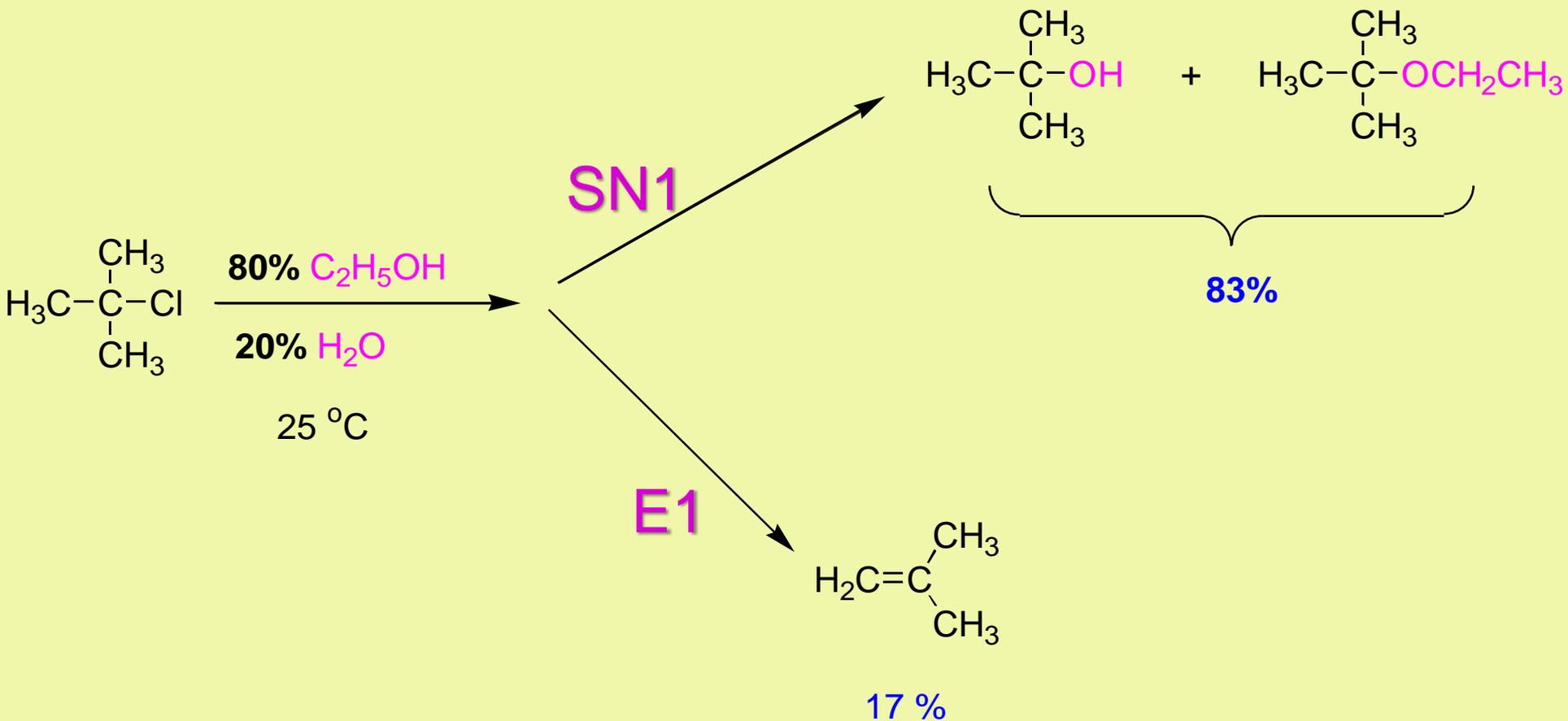
A Closer Look



Reação E1

- Eliminação Unimolecular
- Perda de dois grupos (usualmente X^- and H^+)
- Nucleófilo atua como base
- Fornece, também, produtos S_N1 (mistura)

Competição



- 1º passo: formação do carbocátion

E1

- ◆ Tertiary > Secondary
- ◆ Weak base
- ◆ Good ionizing solvent

- ◆ Rate = $k[\text{halide}]$
- ◆ Saytzeff product
- ◆ No required geometry
- ◆ Rearranged products

or

E2?

- ◆ Tertiary > Secondary
- ◆ Strong base required
- ◆ Solvent polarity not important

- ◆ Rate = $k[\text{halide}][\text{base}]$
- ◆ Saytzeff product
- ◆ Coplanar leaving groups (usually anti)
- ◆ No rearrangements

resumo

Somente reações bimoleculares

$S_N1/E1$ ou $E2$

metila

1º

2º

3º

Reações S_N2

Predomina S_N2

Bases fracas:

I^- , CN^- , RCO_2^-

Predomina S_N2

Não há S_N2

exceção: base forte
impedida

estericamente

Predomina

$E2$

Bases fortes:

(RO^-)

Predomina $E2$

Solvólise: $S_N1/E1$;

baixa temperatura

favorece S_N1

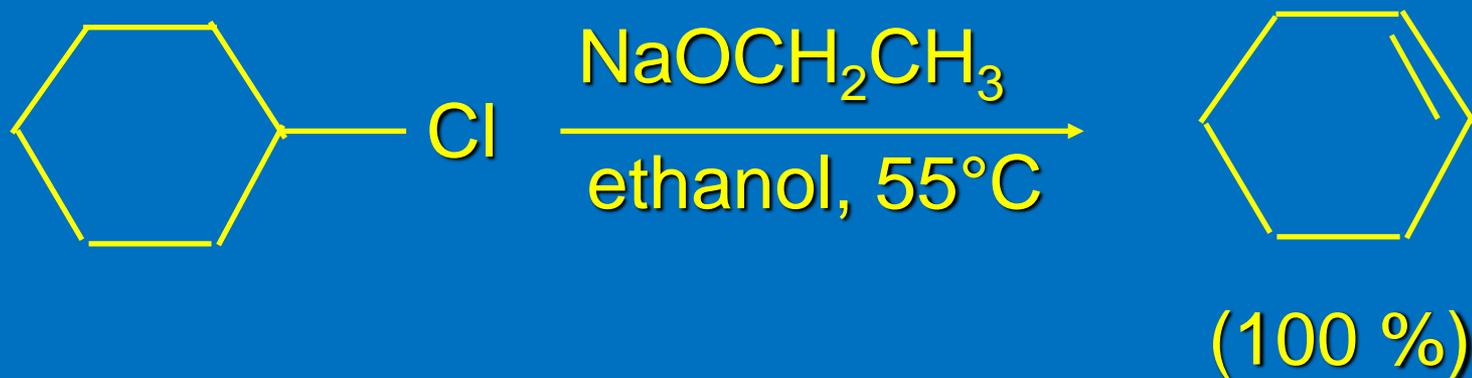
Bases fortes: **(RO^-)**

Predomina

$E2$

Dehydrohalogenation

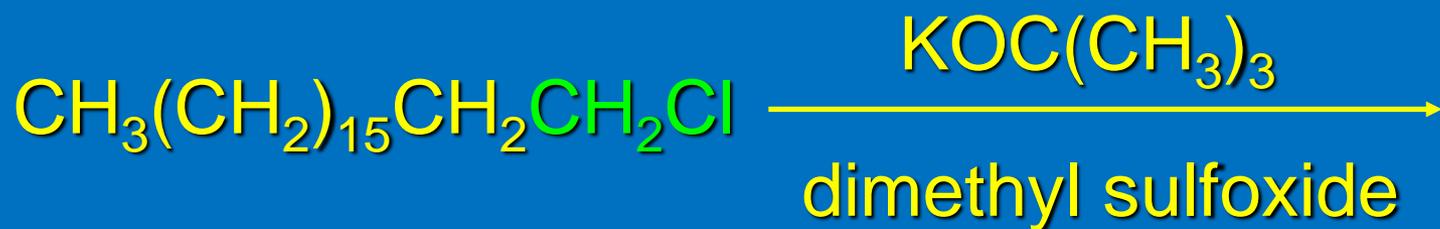
A useful method for the preparation of alkenes



likewise, NaOCH_3 in methanol, or KOH in ethanol

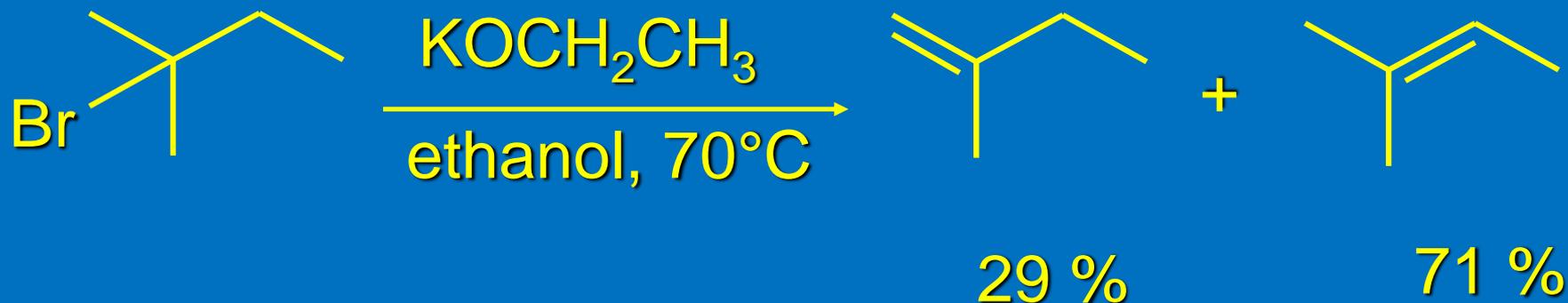
Dehydrohalogenation

When the alkyl halide is **primary**, potassium *tert*-butoxide in dimethyl sulfoxide is the base/solvent system that is normally used.



(86%)

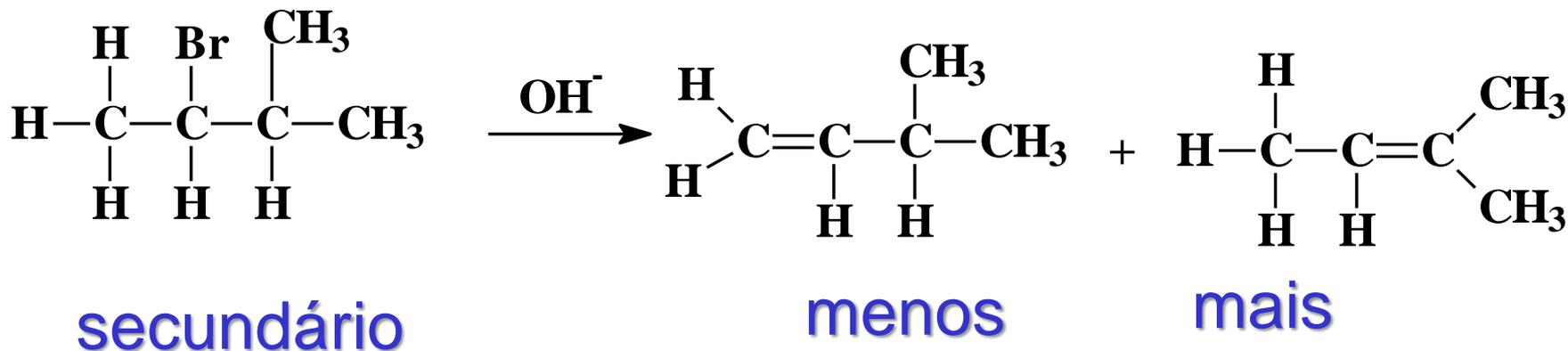
Regioselectivity



follows Zaitsev's (Saytzeff's) rule:
more highly substituted double bond
predominates

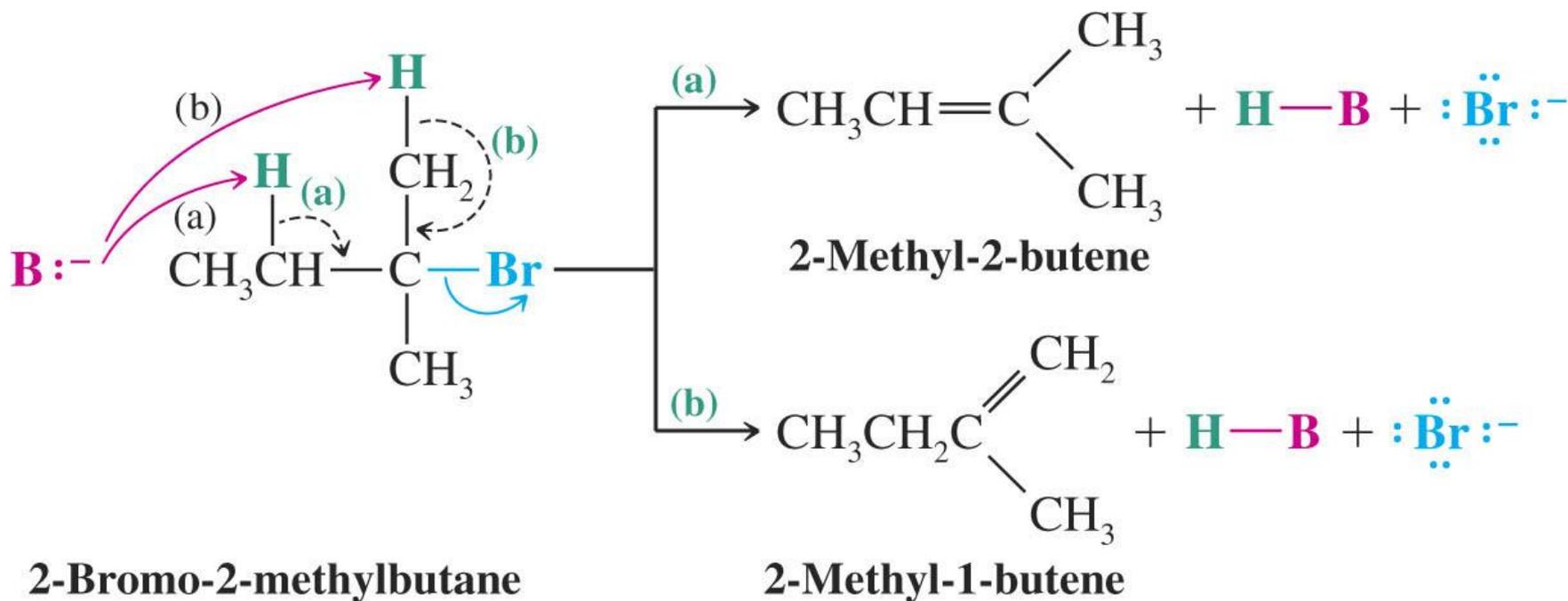
Saytzeff's Rule

- ◆ If more than one elimination product is possible, the most-substituted alkene is the major product (most stable).



- **Zaitsev's Rule: Formation of the Most Substituted Alkene is Favored with a Small Base**

Some hydrogen halides can eliminate to give two different alkene products

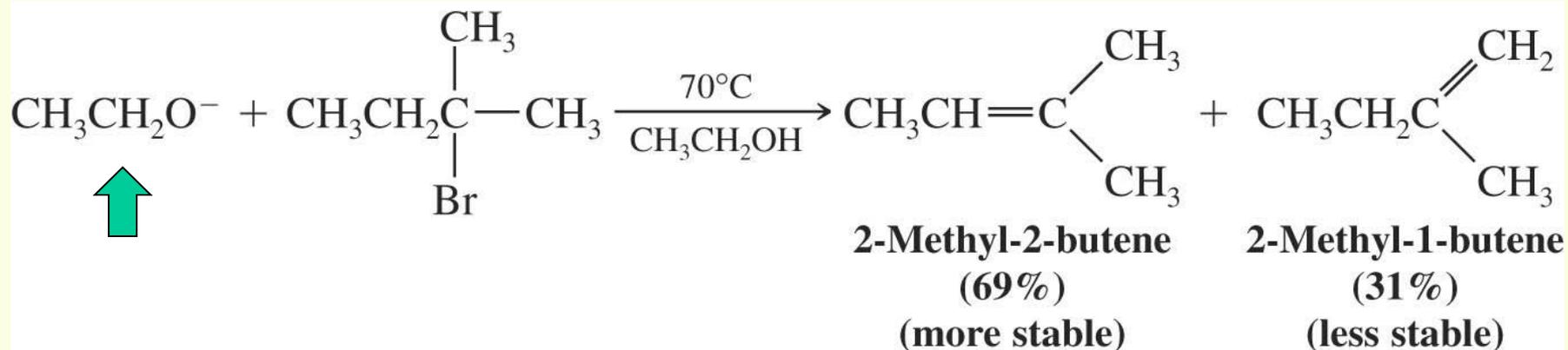


2-Bromo-2-methylbutane

2-Methyl-1-butene

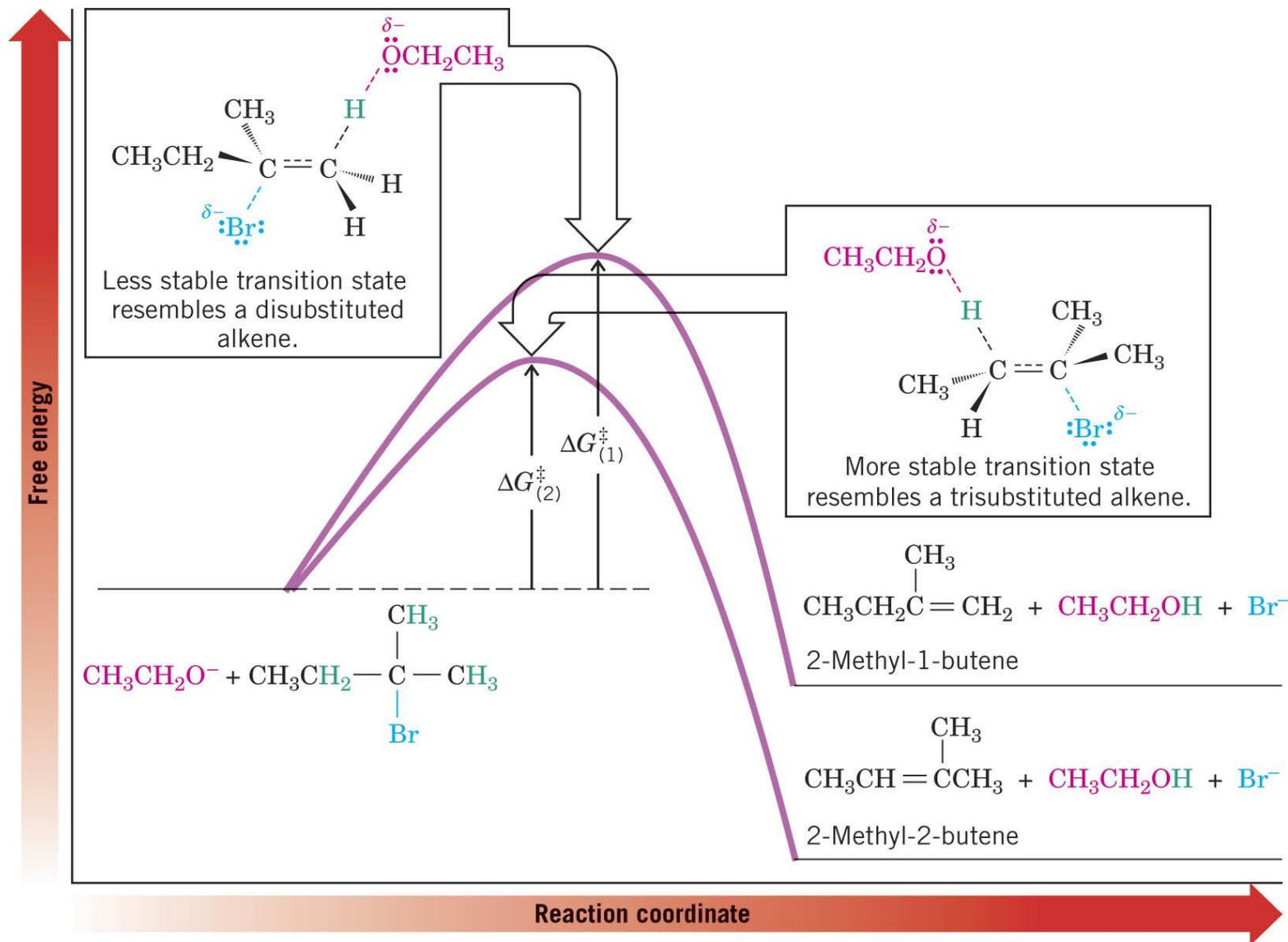
terciário

- **Zaitzev's Rule:** when two different alkene products are possible in an elimination, the most highly substituted (most stable) alkene will be the major product
- This is true only if a small base such as ethoxide is used



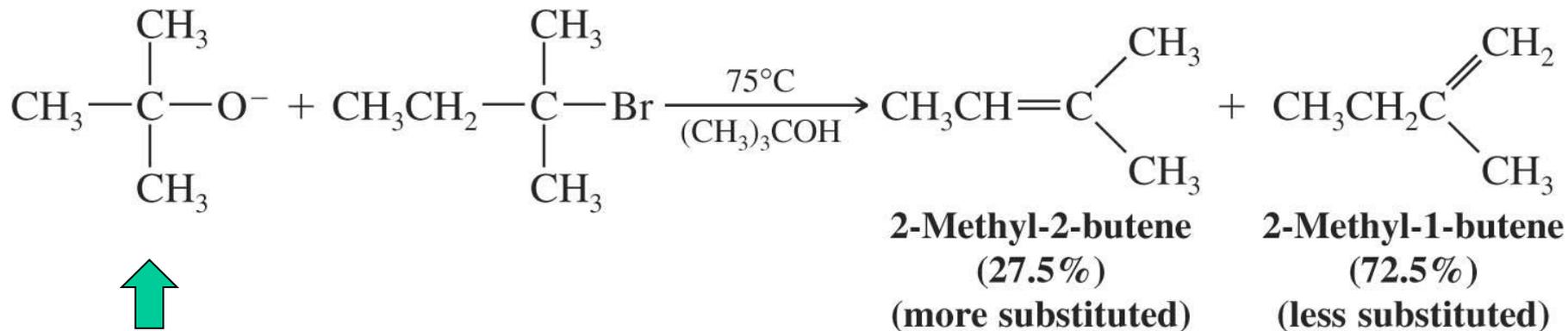
- The transition state in this **E2** reaction has double bond character
- The trisubstituted alkene-like transition state will be most stable and have the lowest ΔG^\ddagger

□ **Kinetic control of product formation:** when one of two products is formed because its free energy of activation is lower and therefore the rate of its formation is higher, this reaction is said to be *under kinetic control*

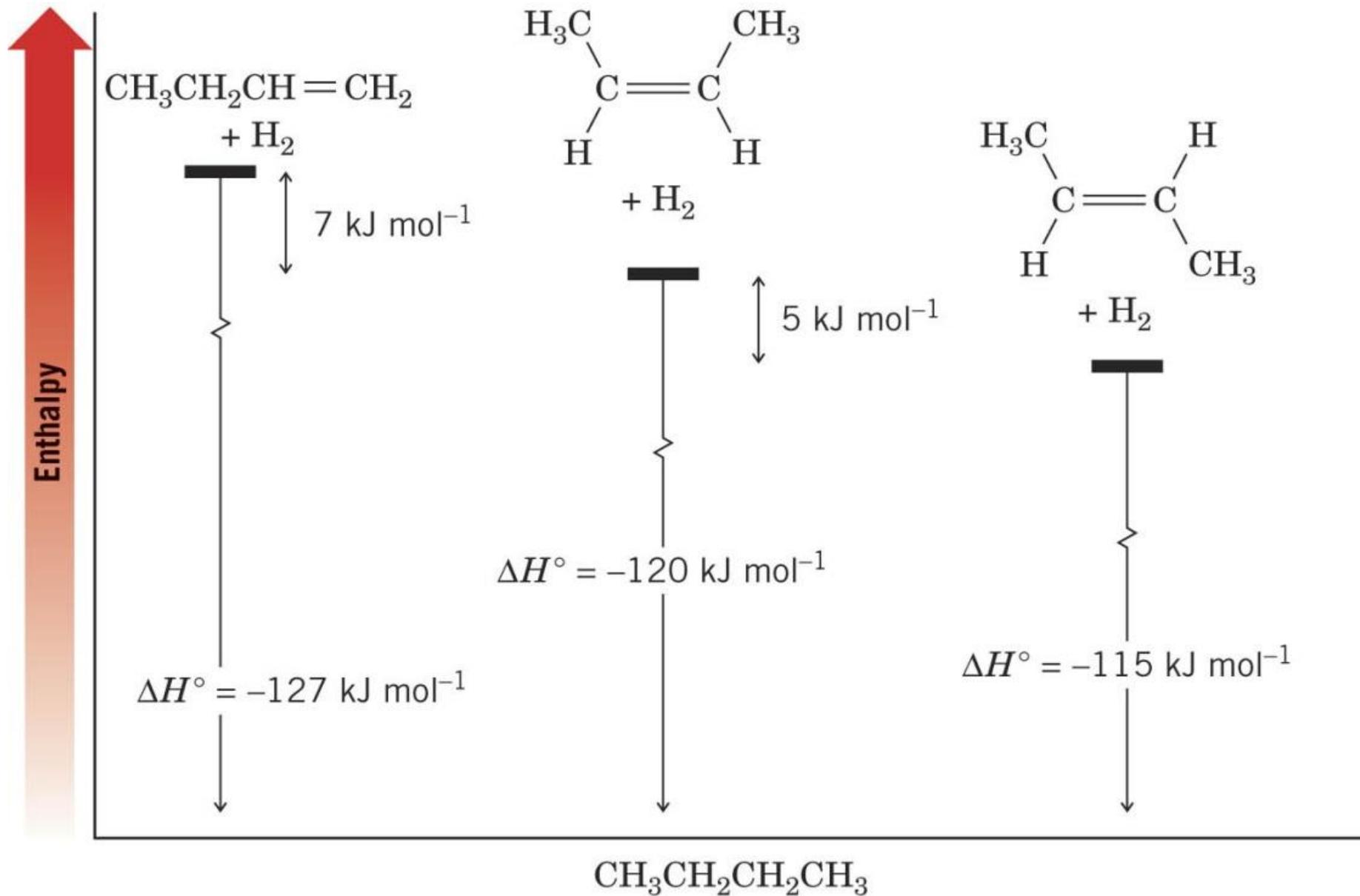


● Formation of the Least Substituted Alkene Using a Bulky Base

Bulky bases such as potassium *tert*-butoxide have difficulty on removing sterically hindered hydrogens and generally only react with more accessible hydrogens (e.g. primary hydrogens)

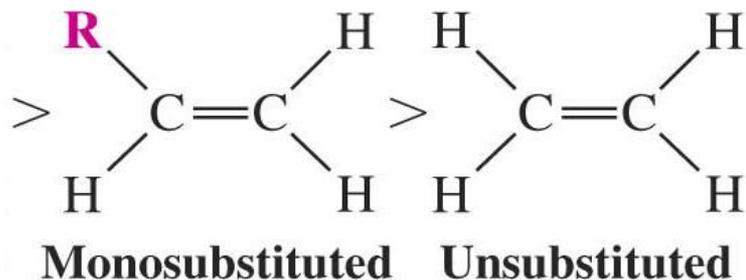
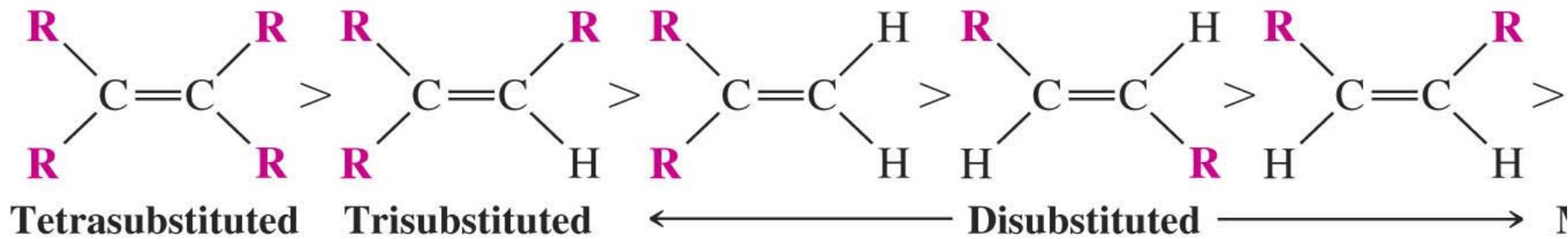


□ Heats of hydrogenation of three butene isomers:



Overall Relative Stabilities of Alkenes

Relative Stabilities of Alkenes



The greater the number of attached alkyl groups (*i.e.* the more highly substituted the carbon atoms of the double bond), the greater the alkene's stability