



QFL0342 - Reatividade dos Compostos Orgânicos

Aula 3. Eliminação- β

Cassius V. Stevani

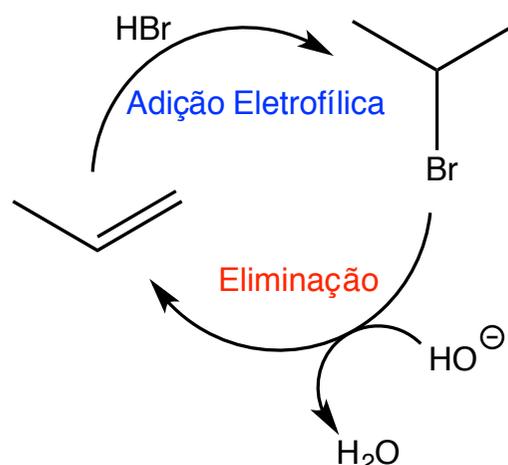


Literatura

Leitura recomendada. Clayden, Greeves, Warren, Wothers, 2ª edição, cap. 17

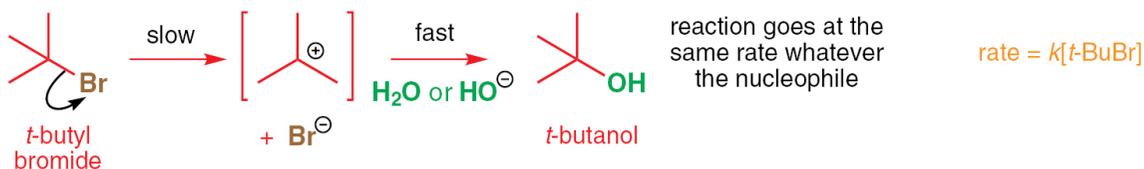
Substituição e eliminação

- Reações de eliminação levam à formação de alcenos. Alcenos, por sua vez, reagem formando produtos que podem sofrer eliminação.

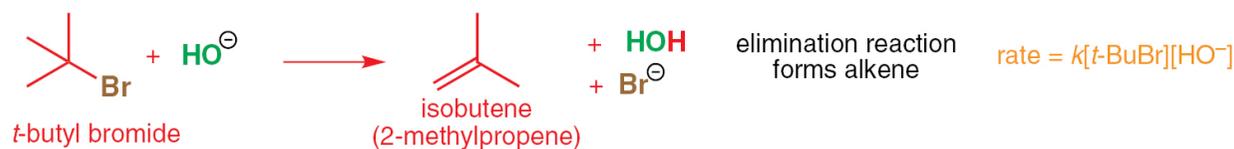


- Os dois tipos mais comuns de mecanismo de eliminação são E1 e E2.

nucleophilic substitution reactions of *t*-BuBr

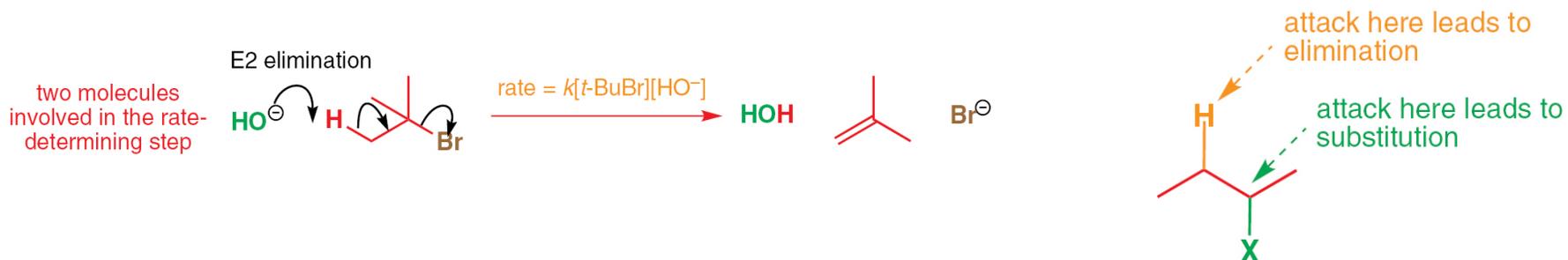


reaction of *t*-BuBr with concentrated solution of NaOH

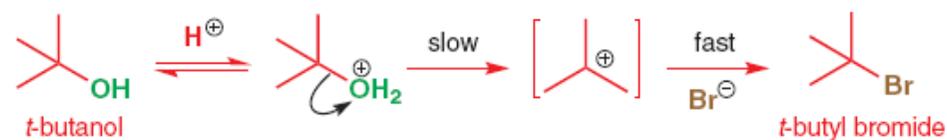


Eliminação E2 e E1 | Mecanismos

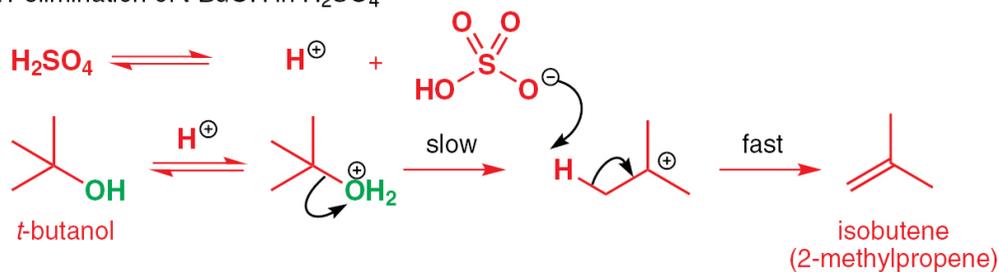
- Eliminação pode ocorrer na presença de base ou ácido.



nucleophilic substitution of *t*-BuOH with HBr



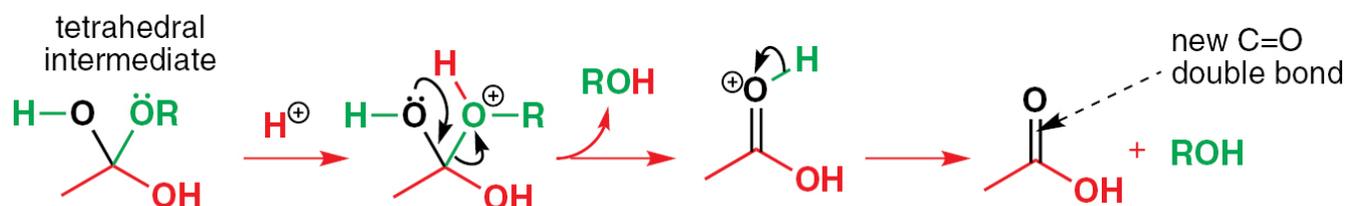
E1 elimination of *t*-BuOH in H_2SO_4



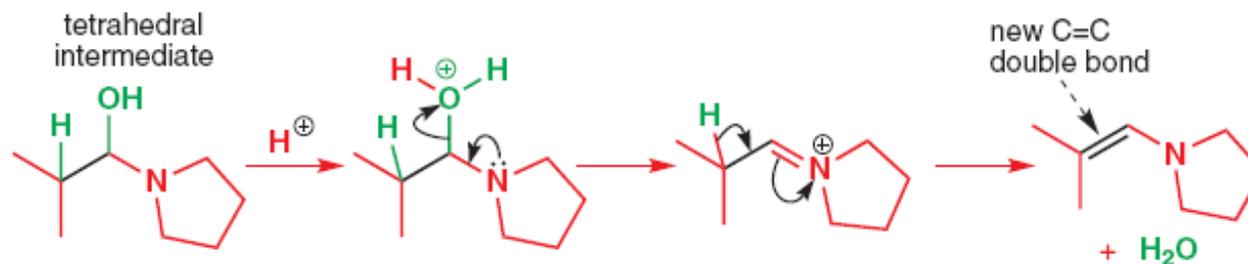
Eliminação E1 | Outros exemplos

- Eliminação E1 pode ocorrer na hidrólise de ésteres e formação de enamina.

E1 elimination of ROH during ester hydrolysis



E1 elimination of H₂O during enamine formation

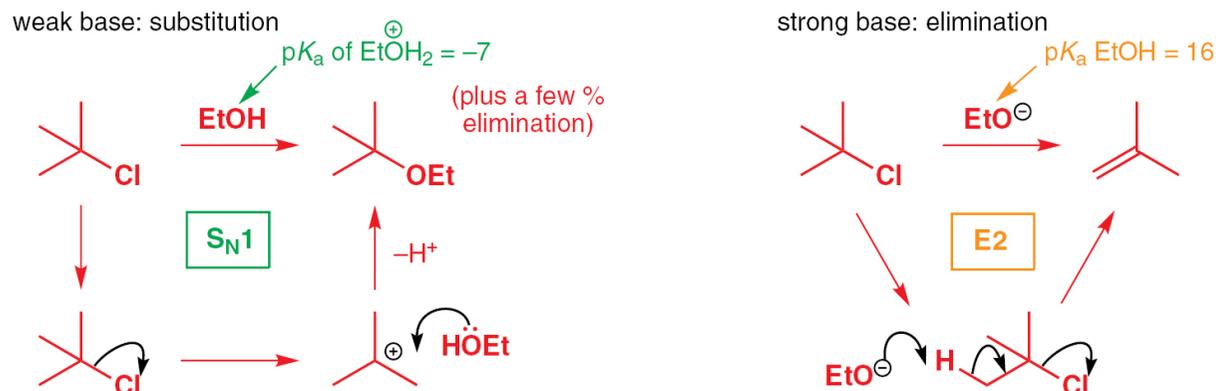




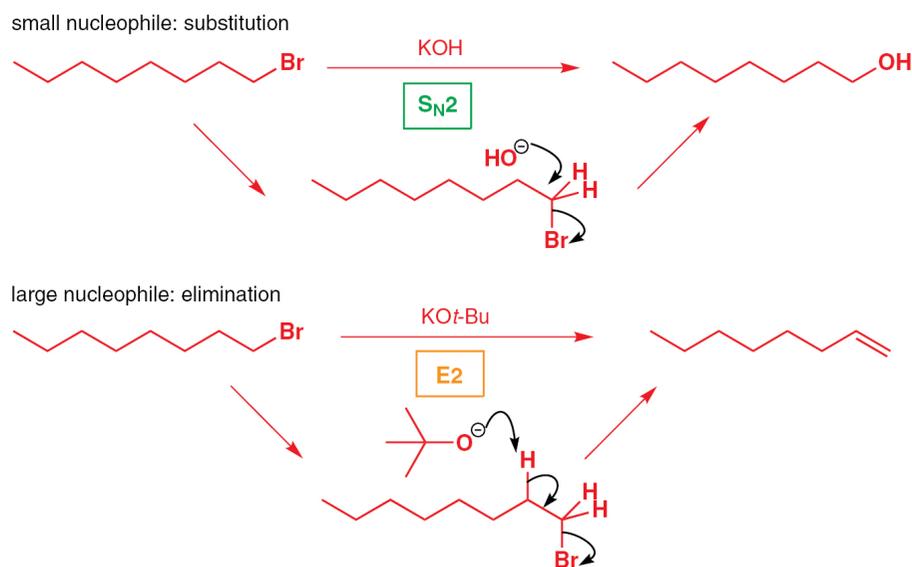
Eliminação-β

Eliminação vs. Substituição | Força e tamanho da base

- A força da base afeta o caminho da reação.



- O tamanho da base afeta o caminho da reação.



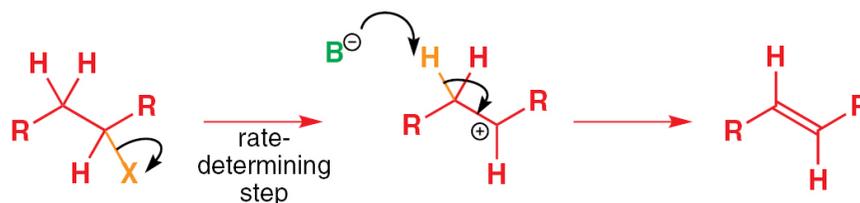
Eliminação vs. Substituição | Temperatura

- Nucleófilos que são bases fortes favorecem eliminação em comparação com substituição.
- Bases volumosas favorecem eliminação.
- Temperaturas altas favorecem E2.

E1 vs. E2

- Mecanismo geral E1.

general mechanism for E1 elimination



$$\text{rate} = k[\text{alkyl halide}]$$

general mechanism for E2 elimination



$$\text{rate} = k[\text{B}^-][\text{alkyl halide}]$$

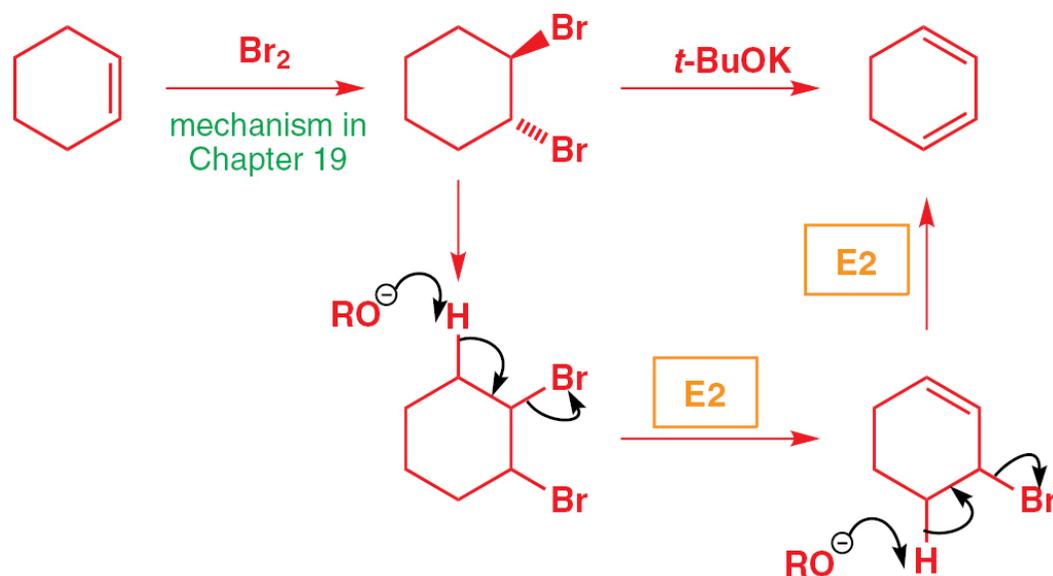
- Inúmeros fatores podem fazer com que uma eliminação ocorra via E1 ou E2.
- Bases volumosas favorecem E2.



Eliminação-β

E2 | Exemplo

synthesis of a diene by a double E2 elimination



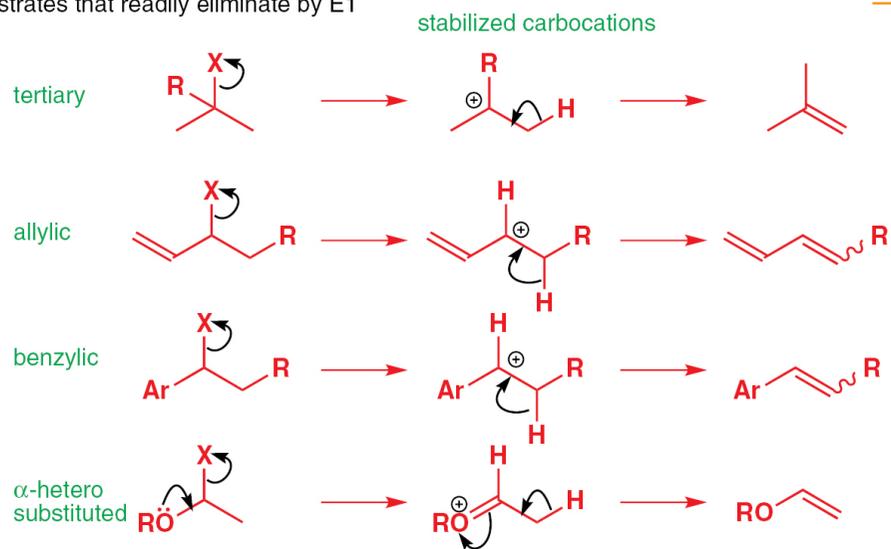


Eliminação-β

E1 vs. E2

- A estrutura do substrato pode favorecer E1. A formação de um carbocátion estável pode favorecer E1.

substrates that readily eliminate by E1



may also eliminate by E2

substrates that may eliminate by E1



substrates that never eliminate by E1

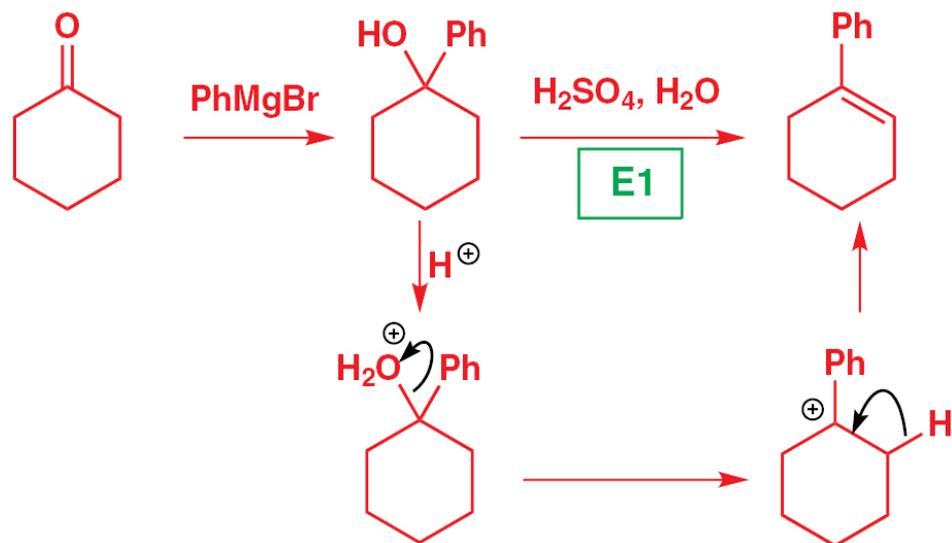


substrates that cannot eliminate by either mechanism—no appropriately placed hydrogens

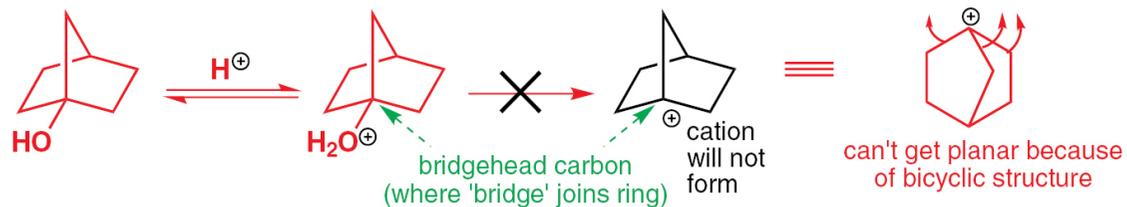


cannot eliminate by E2

E1 | Exemplo



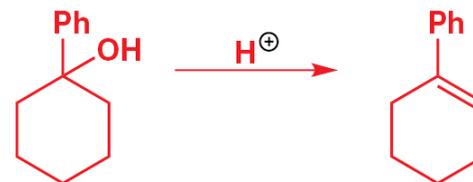
- Cuidado com casos envolvendo estruturas bicíclicas.



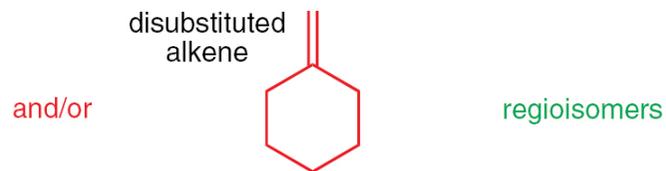
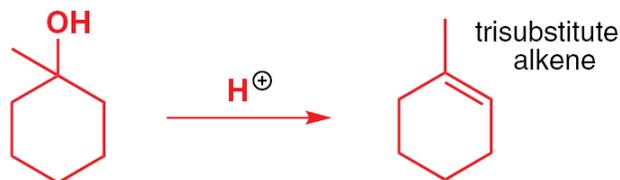
E1 | Estereoquímica

- Regioquímica e estereoquímica.

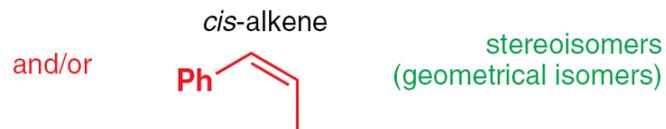
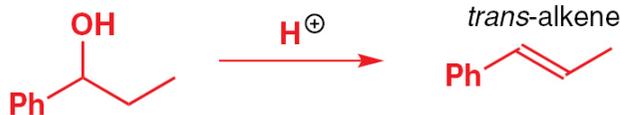
only one alkene possible



two regioisomeric alkenes possible

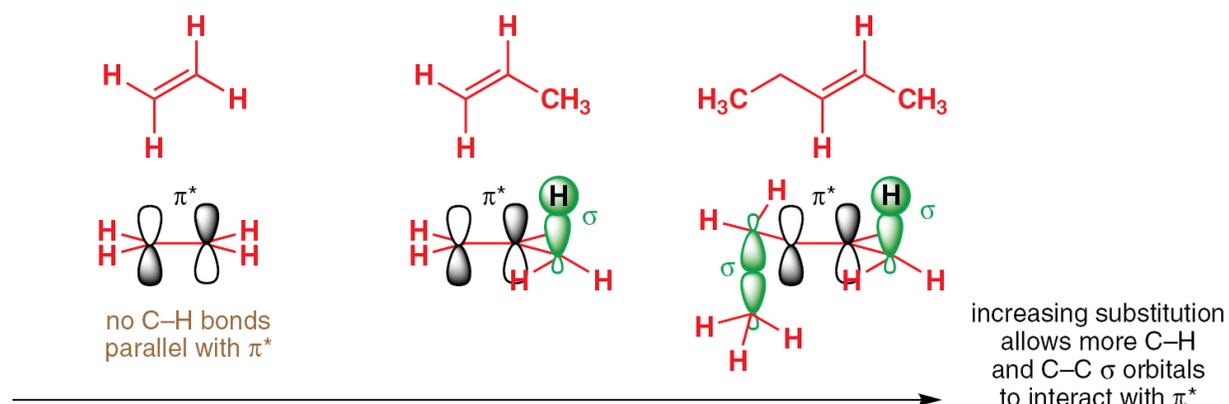
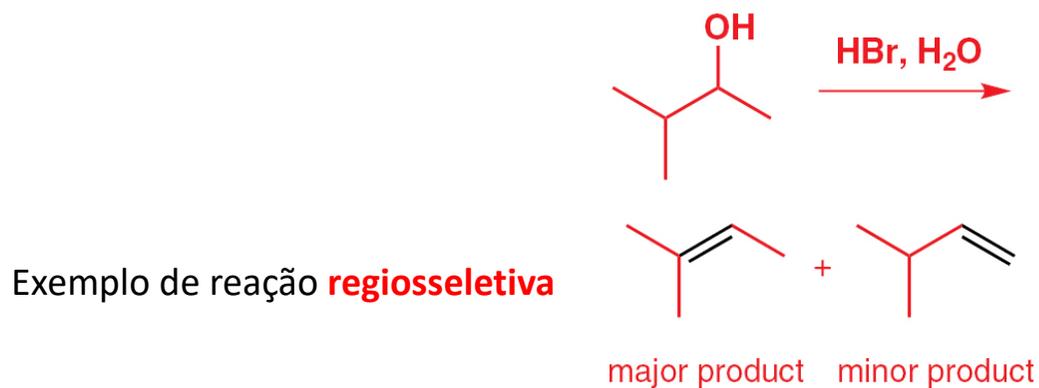


two stereoisomeric alkenes possible



E1 | Estereoquímica

- Alcenos mais substituídos são mais estáveis, devido à hiperconjugação.



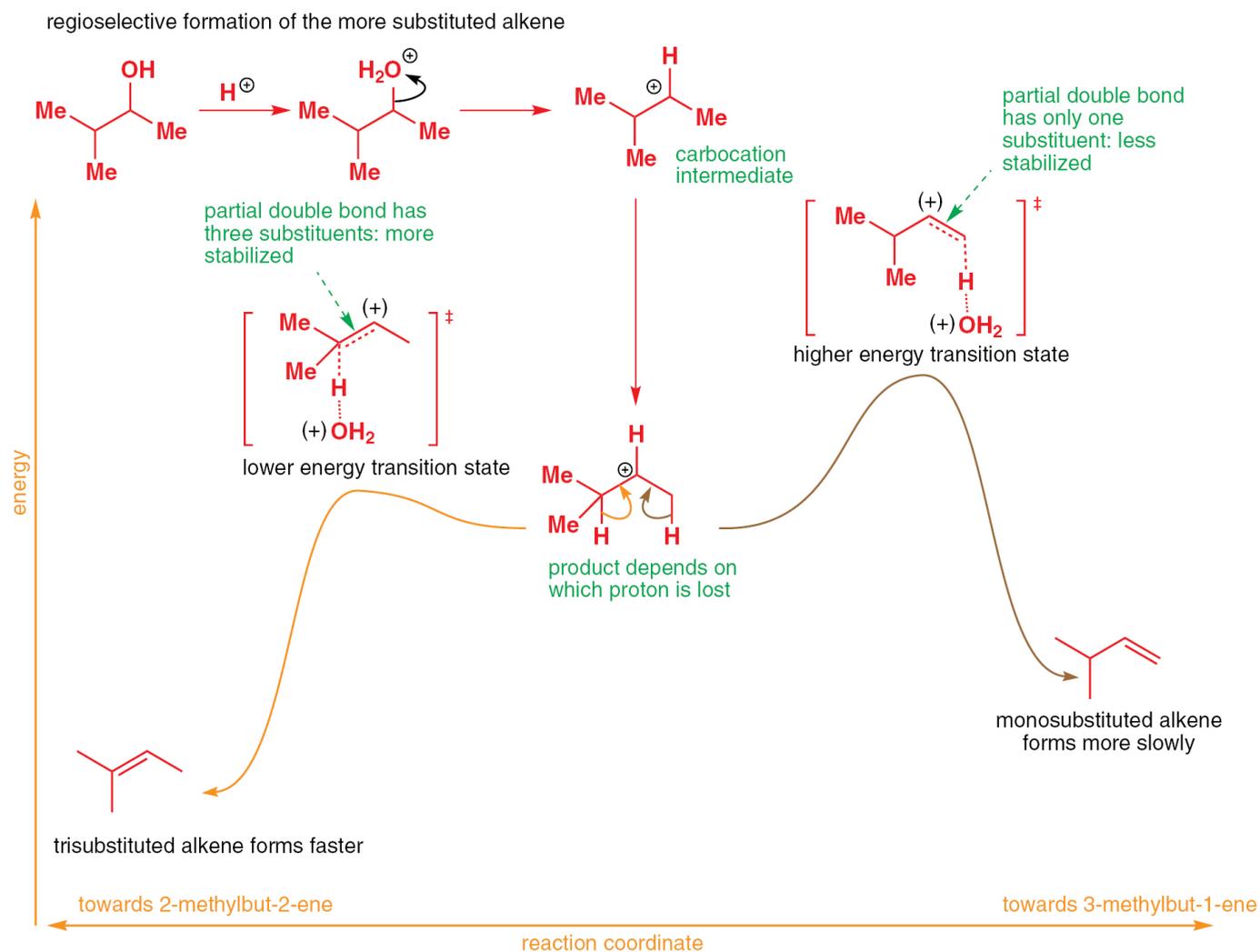


Eliminação-β

E1 | Estereoquímica

Exemplo de reação **regiosseletiva**

Um dos regioisômeros se forma em maior quantidade

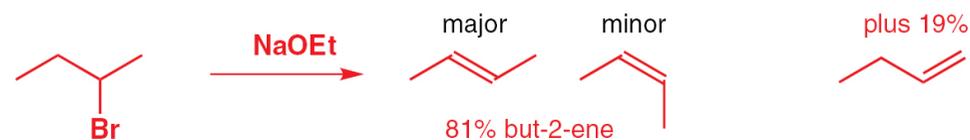
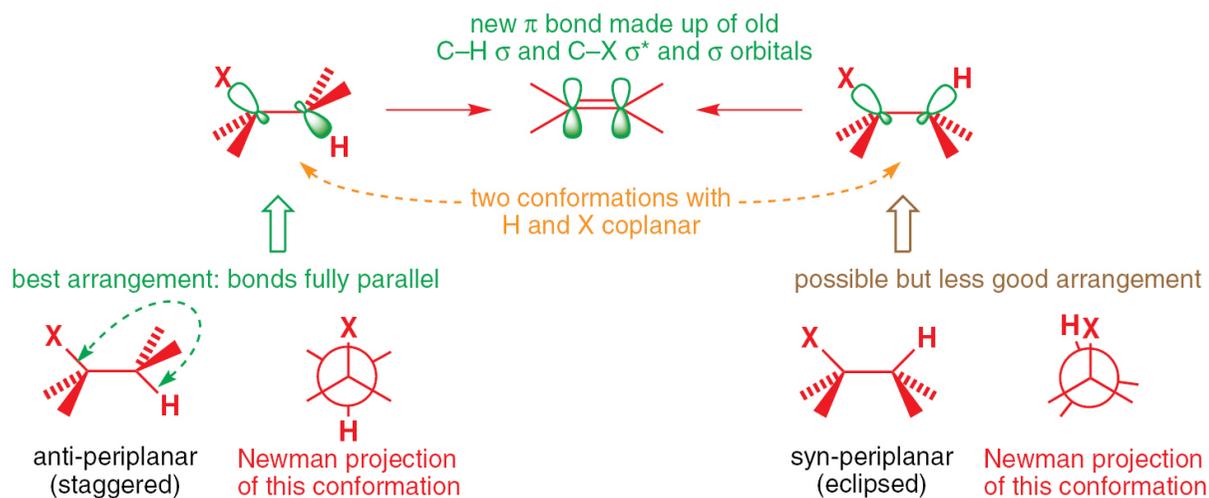




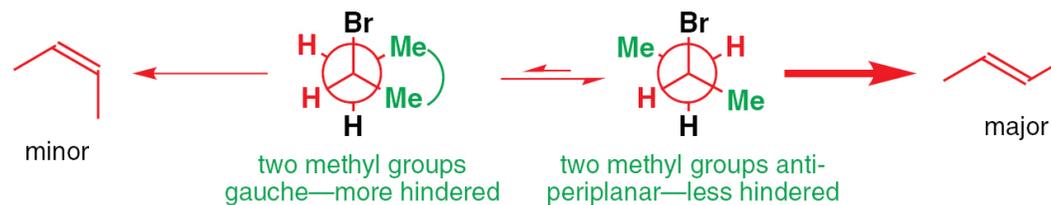
Eliminação-β

E2 | Estereoquímica

- Estado de transição E2 é antiperiplanar.



H and Br must be anti-periplanar for E2 elimination:
two possible conformations

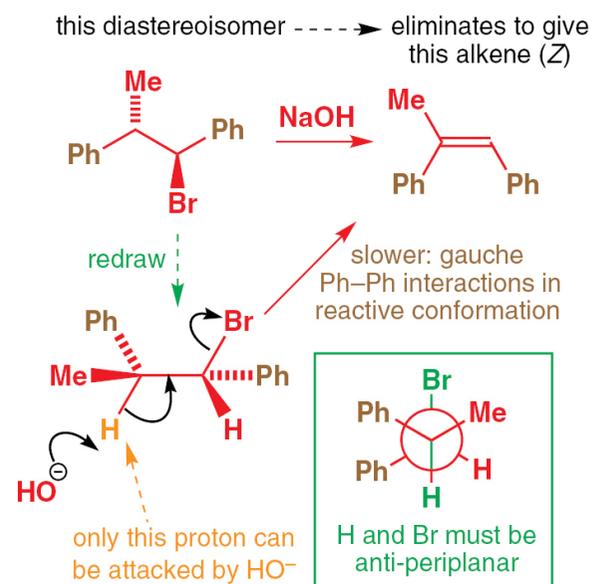
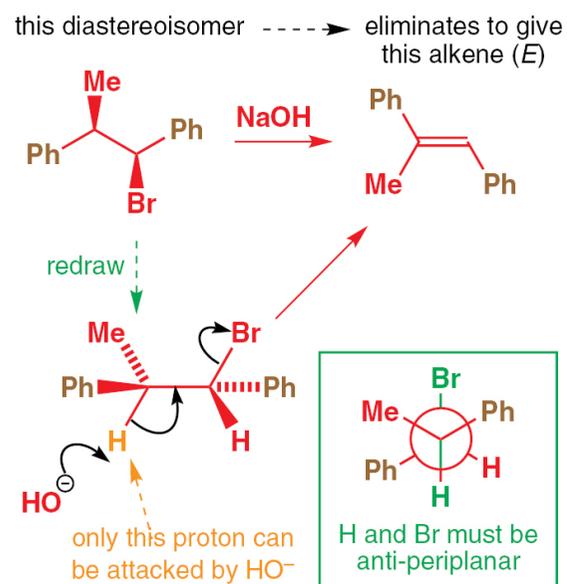




Eliminação-β

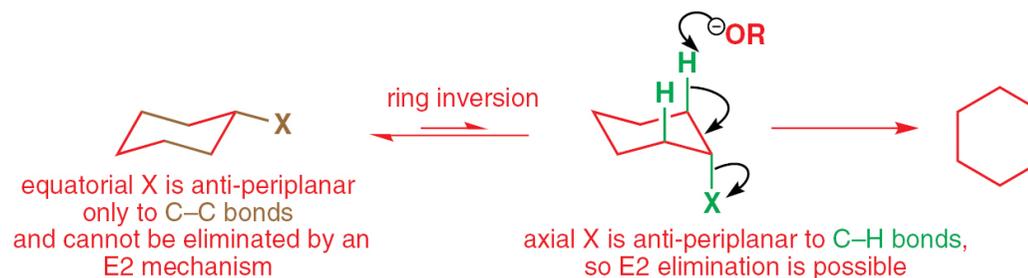
E2 | Estereoquímica

- E2 pode ser estereoespecífica: só se forma um único estereoisômero.

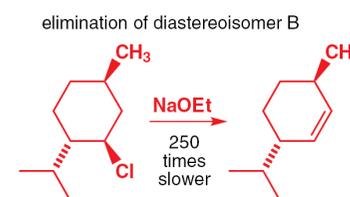
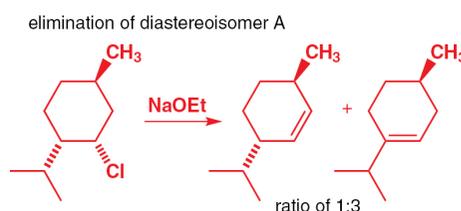


Eliminação em cicloexanos

- E2 pode ser estereoespecífica: só se forma um único estereoisômero.

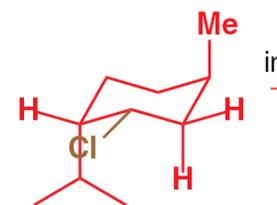


Mecanismo só pode ser E2
Qual seria o produto por E1?



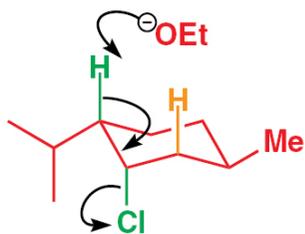
conformation of diastereoisomer A

No C-H bonds anti-periplanar to the C-Cl bond: no elimination



ring inversion

two anti-periplanar C-H bonds: either can eliminate to give different products



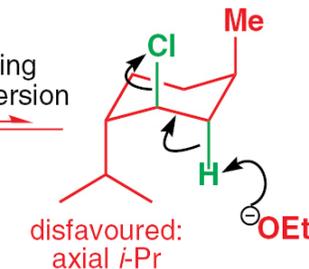
conformation of diastereoisomer B

No C-H bonds anti-periplanar to the C-Cl bond: no elimination



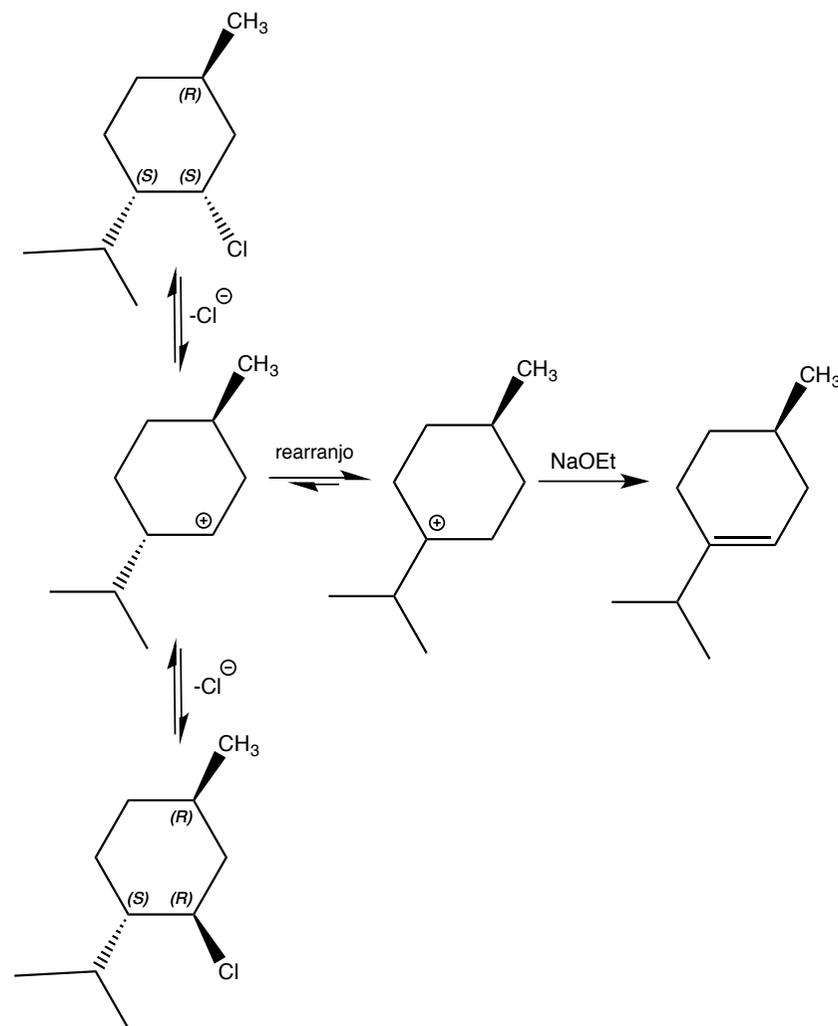
ring inversion

one anti-periplanar C-H bond: single alkene formed



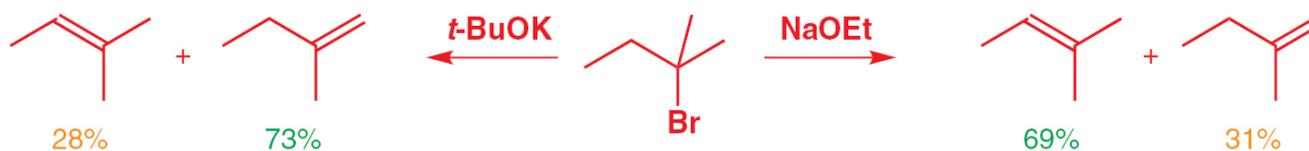
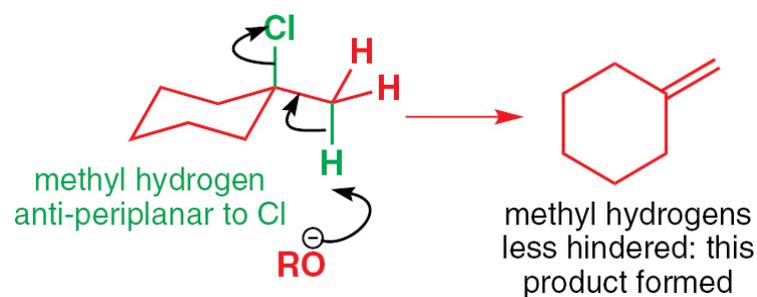
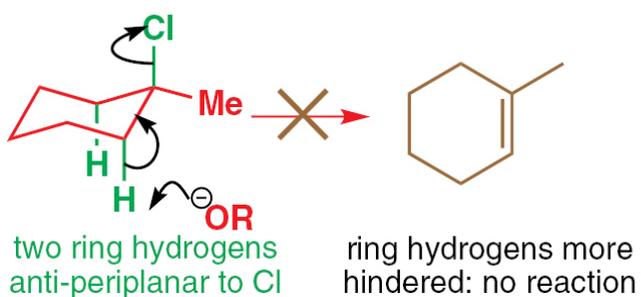
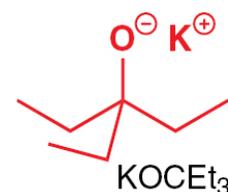
Eliminação em cicloexanos

- Produto de A e B via E1.



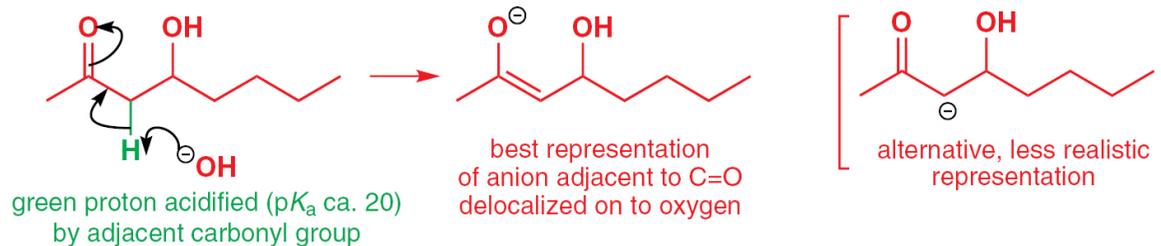
E2 | Estereoquímica

- Regiosseletividade. Uso de base forte e impedida pode levar ao alceno menos estável.



E1cb

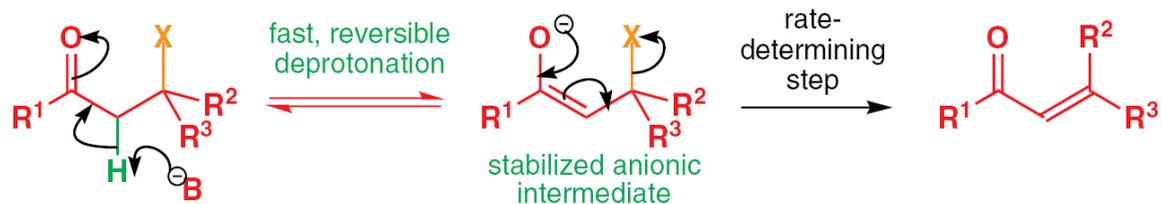
- Eliminação E1 via base conjugada, E1cb. Acontece quando o grupo abandonador é ruim.



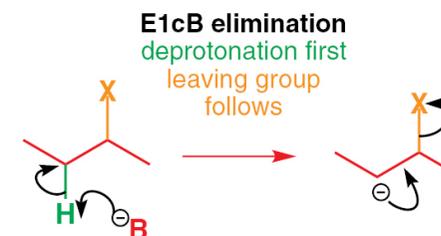
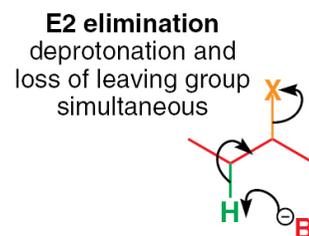
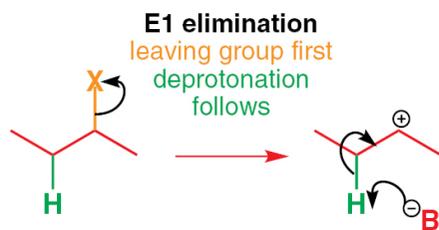
the elimination step
by the E1cB mechanism



the E1cB mechanism



Resumo



		Poor nucleophile (e.g. H ₂ O, ROH)	Weakly basic nucleophile (e.g. I ⁻ , RS ⁻)	Strongly basic, unhindered nucleophile (e.g. RO ⁻)	Strongly basic, hindered nucleophile (e.g. DBU, t-BuO ⁻)
methyl	<chem>H3C-X</chem>	no reaction	S _N 2	S _N 2	S _N 2
primary (unhindered)	<chem>CH3CH2CH2-X</chem>	no reaction	S _N 2	S _N 2	E2
primary (hindered)	<chem>CH3CH(CH3)CH2-X</chem>	no reaction	S _N 2	E2	E2
secondary	<chem>CH3CH(CH3)CH2-X</chem>	S _N 1, E1 (slow)	S _N 2	E2	E2
tertiary	<chem>CH3C(CH3)2CH2-X</chem>	E1 or S _N 1	S _N 1, E1	E2	E2
β to anion-stabilizing group	<chem>CH3C(=O)CH2CH2-X</chem> α β	E1cB	E1cB	E1cB	E1cB