5.14

Dehydrohalogenation of Alkyl Halides

b-Elimination Reactions Overview

dehydrogenation of alkanes:

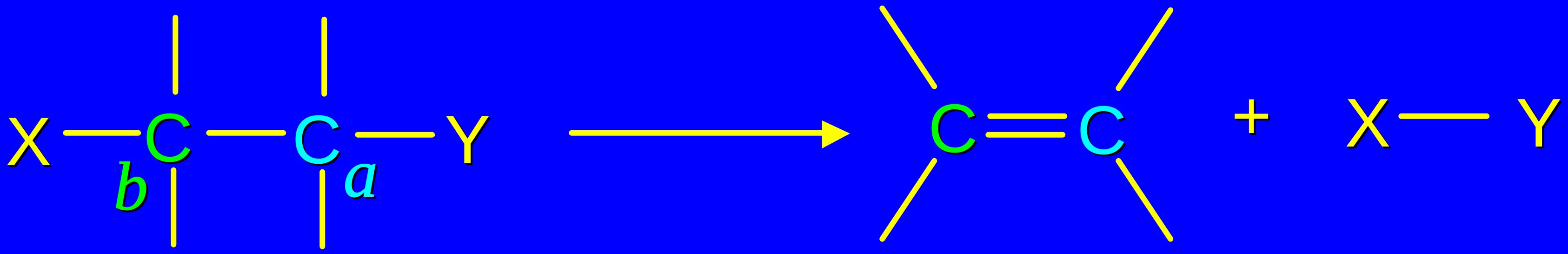
X = Y = H

dehydration of alcohols:

X = H; Y = OH

dehydrohalogenation of alkyl halides:

X = H; Y = Br, etc.



b-Elimination Reactions Overview

dehydrogenation of alkanes:

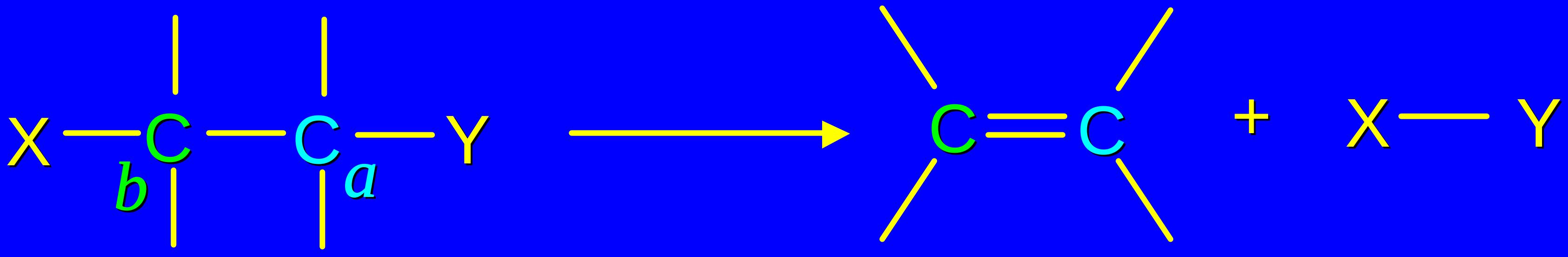
industrial process; not regioselective

dehydration of alcohols:

acid-catalyzed

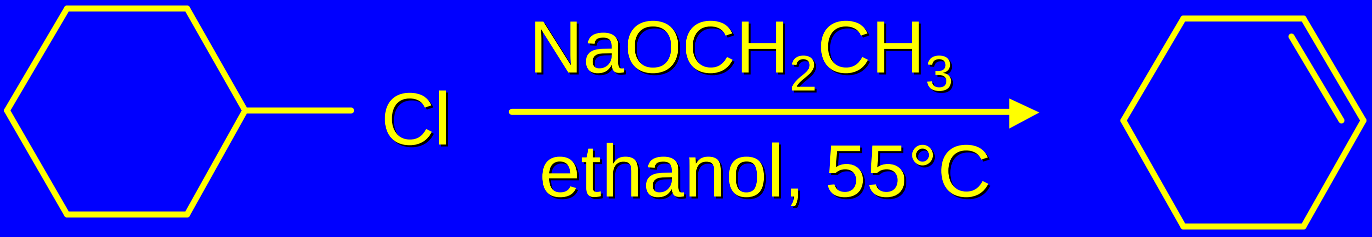
dehydrohalogenation of alkyl halides:

consumes base



Dehydrohalogenation

is a useful method for the preparation of alkenes



(100 %)

likewise, $NaOCH_3$ in methanol, or KOH in ethanol

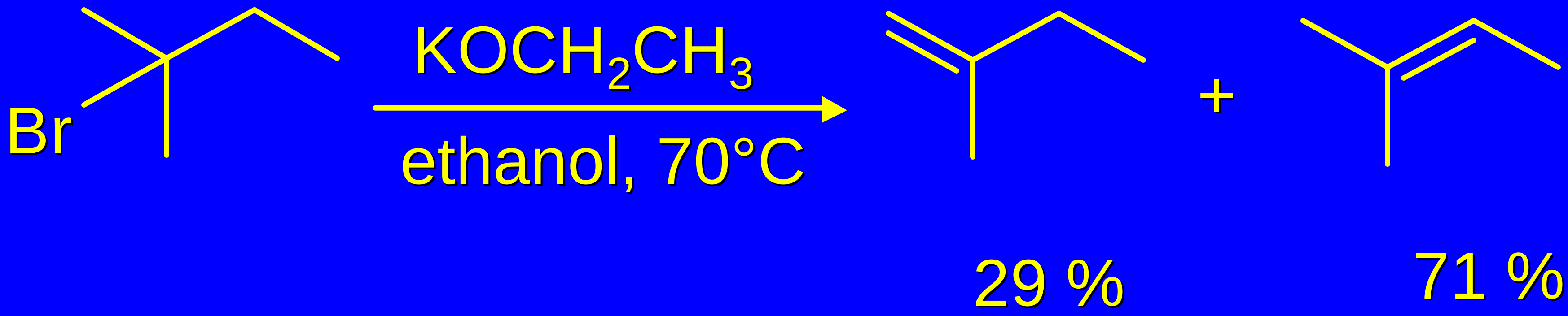
Dehydrohalogenation

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

$$CH_3(CH_2)_{15}CH_2CH_2Cl \xrightarrow[\text{dimethyl sulfoxide}]{KOC(CH_3)_3} CH_3(CH_2)_{15}CH{=}CH_2$$

(86%)

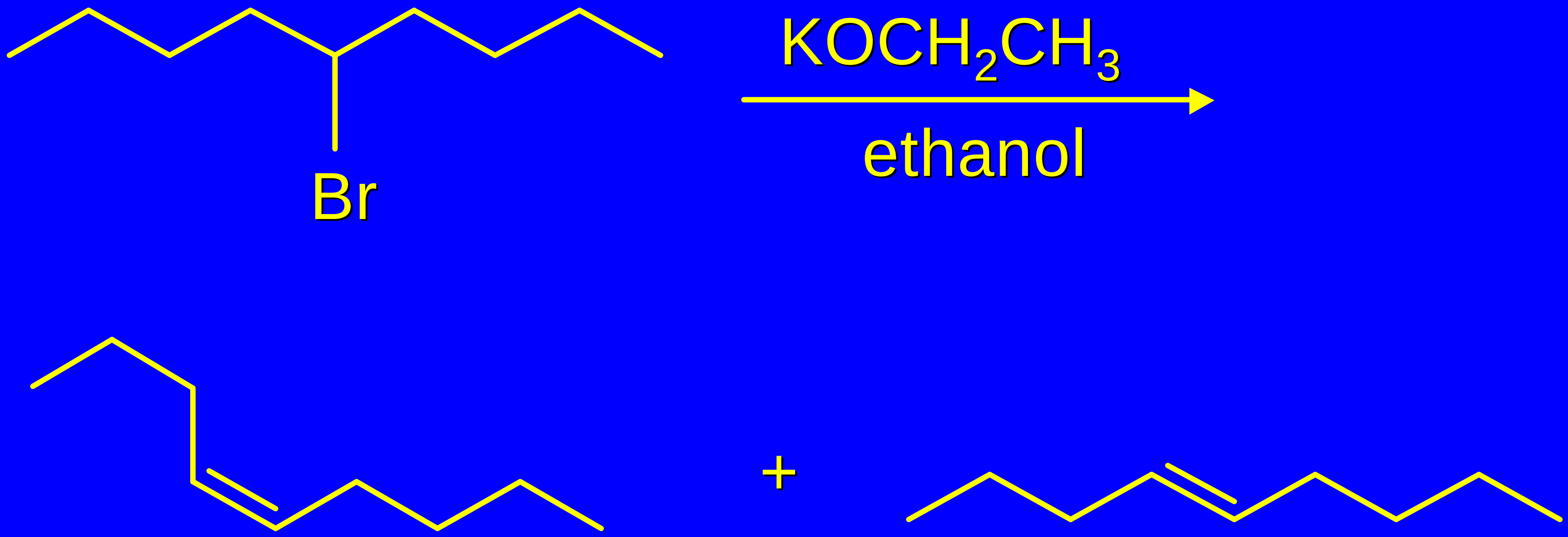
Regioselectivity



follows Zaitsev's rule

more highly substituted double bond predominates

Stereoselectivity



Br

$\xrightarrow[\text{ethanol}]{KOCH_2CH_3}$

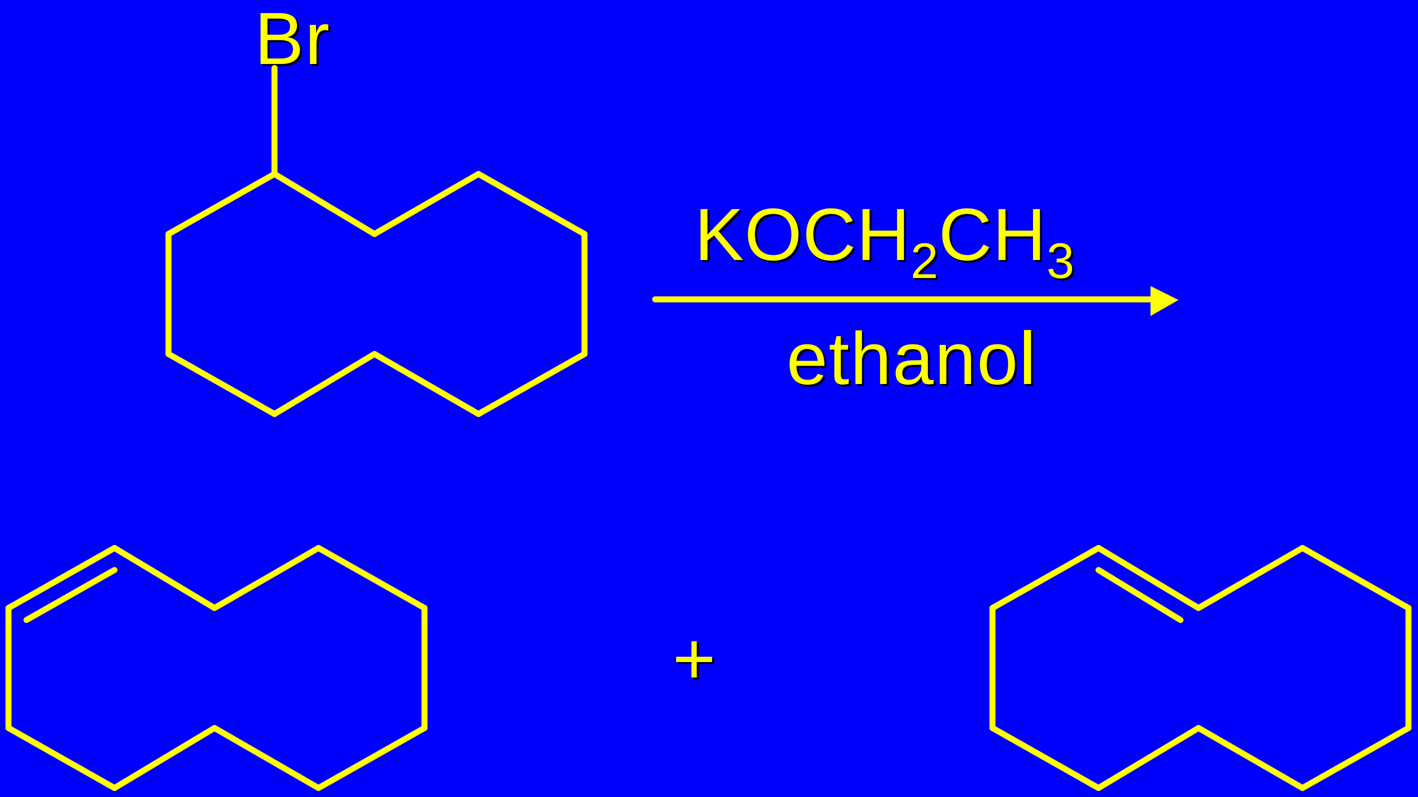
\+

(23%)

(77%)

more stable configuration
of double bond predominates

Stereoselectivity



(85%) (15%)

more stable configuration
of double bond predominates

5.15

Mechanism of the Dehydrohalogenation of Alkyl Halides: The E2 Mechanism

Facts

(1) Dehydrohalogenation of alkyl halides exhibits second-order kinetics

first order in alkyl halide
first order in base
rate = *k*[alkyl halide][base]

implies that rate-determining step involves both base and alkyl halide; i.e., it is bimolecular

Facts

(2) Rate of elimination depends on halogen

weaker C—X bond; faster rate

rate: RI > RBr > RCl > RF

implies that carbon-halogen bond breaks in the rate-determining step

The E2 Mechanism

concerted (one-step) bimolecular process

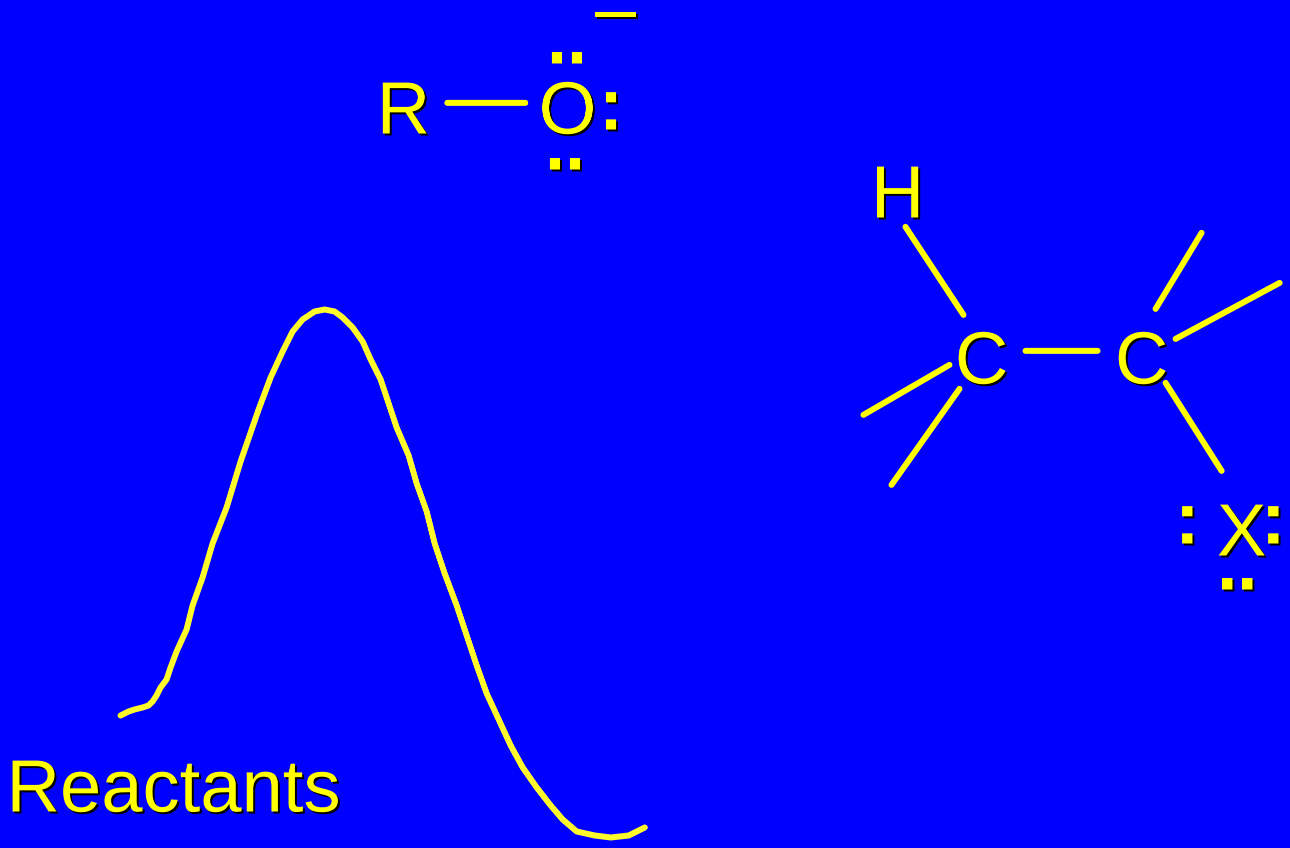
single transition state

C—H bond breaks

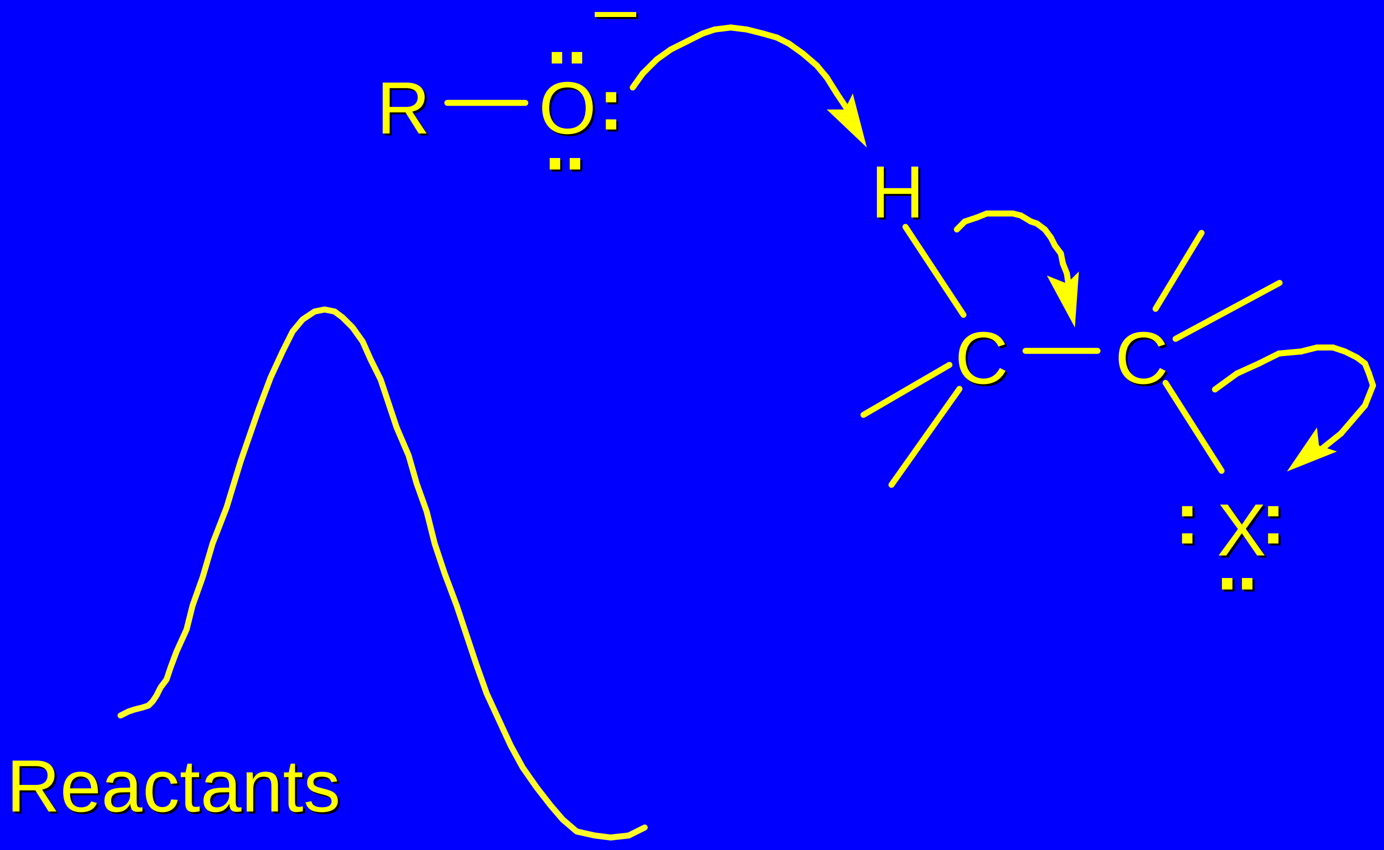
π component of double bond forms

C—X bond breaks

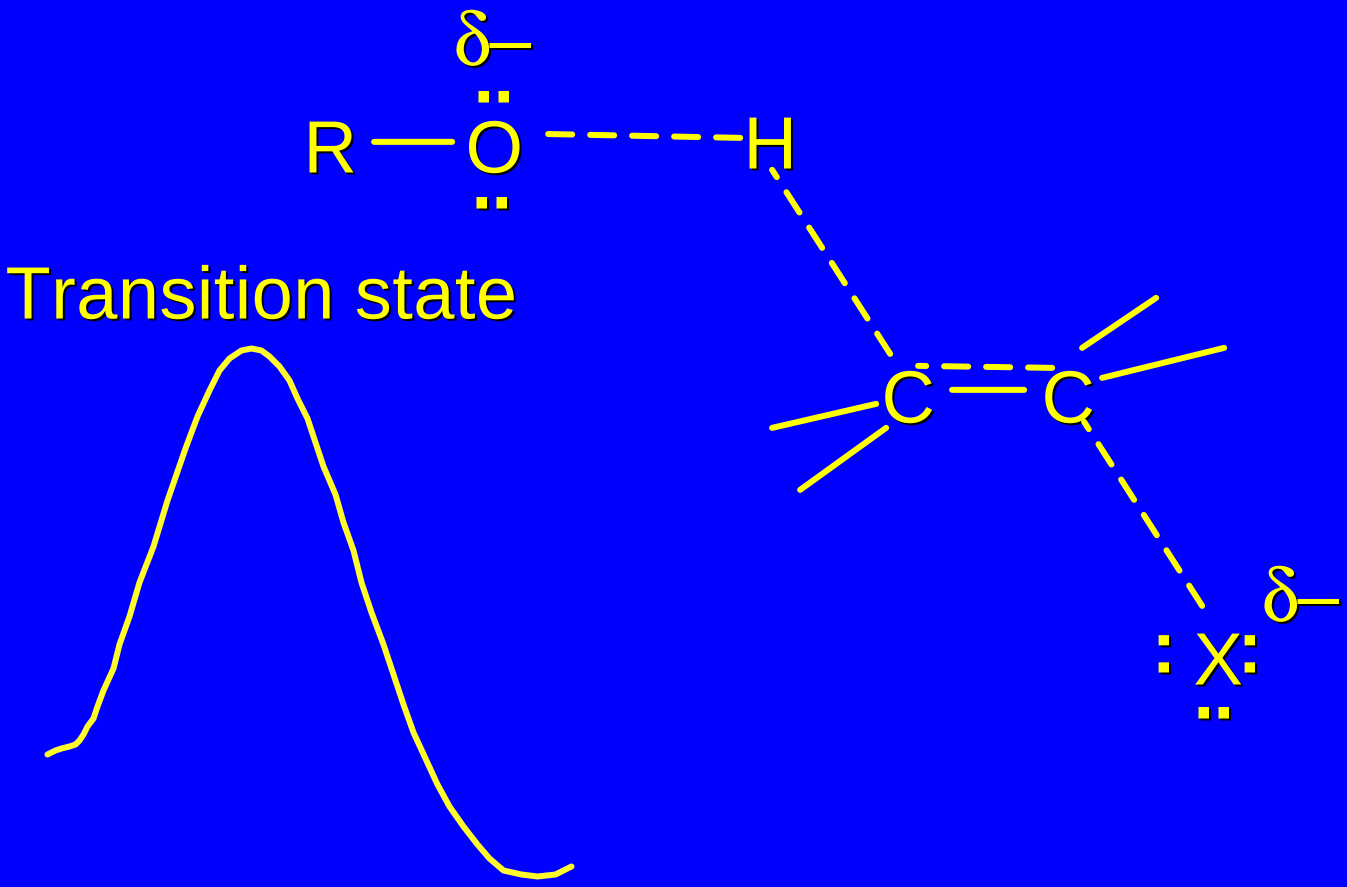
The E2 Mechanism



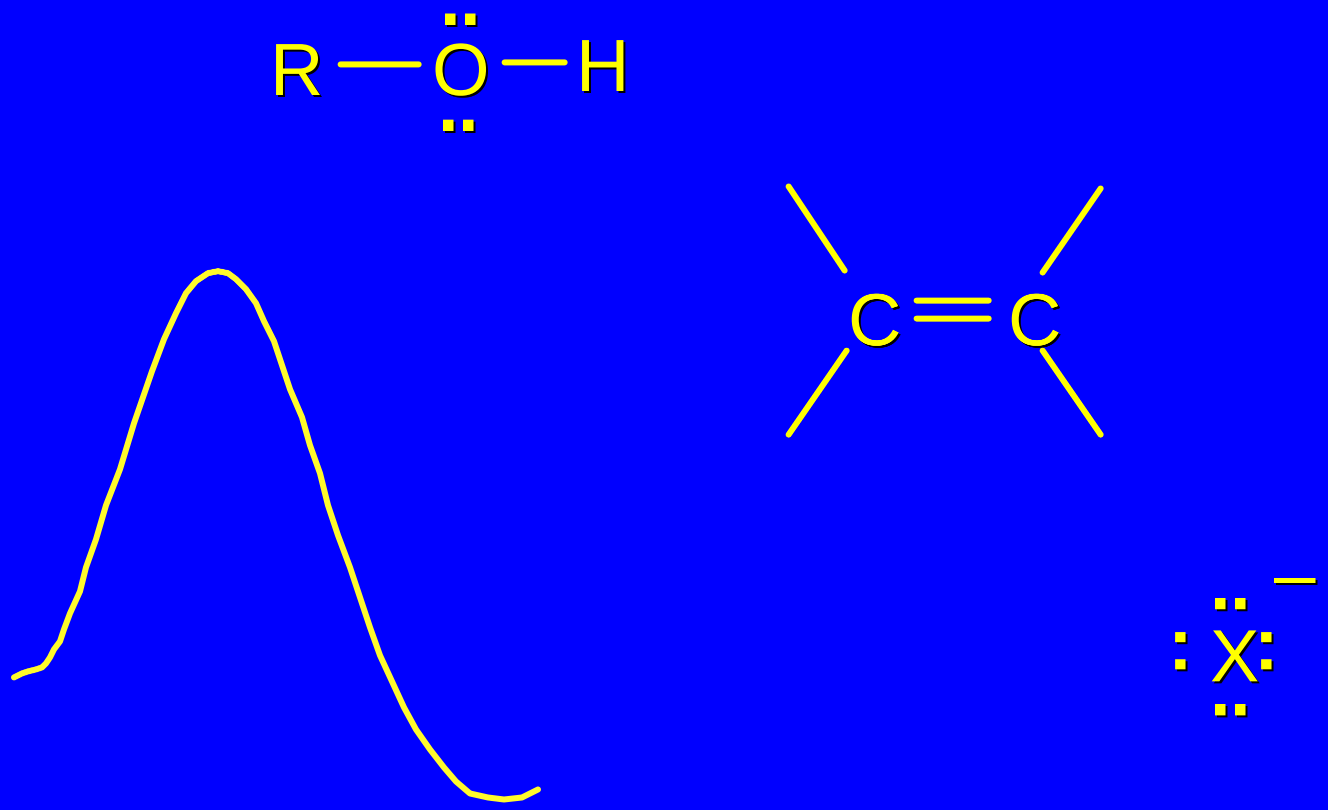
The E2 Mechanism



The E2 Mechanism



The E2 Mechanism



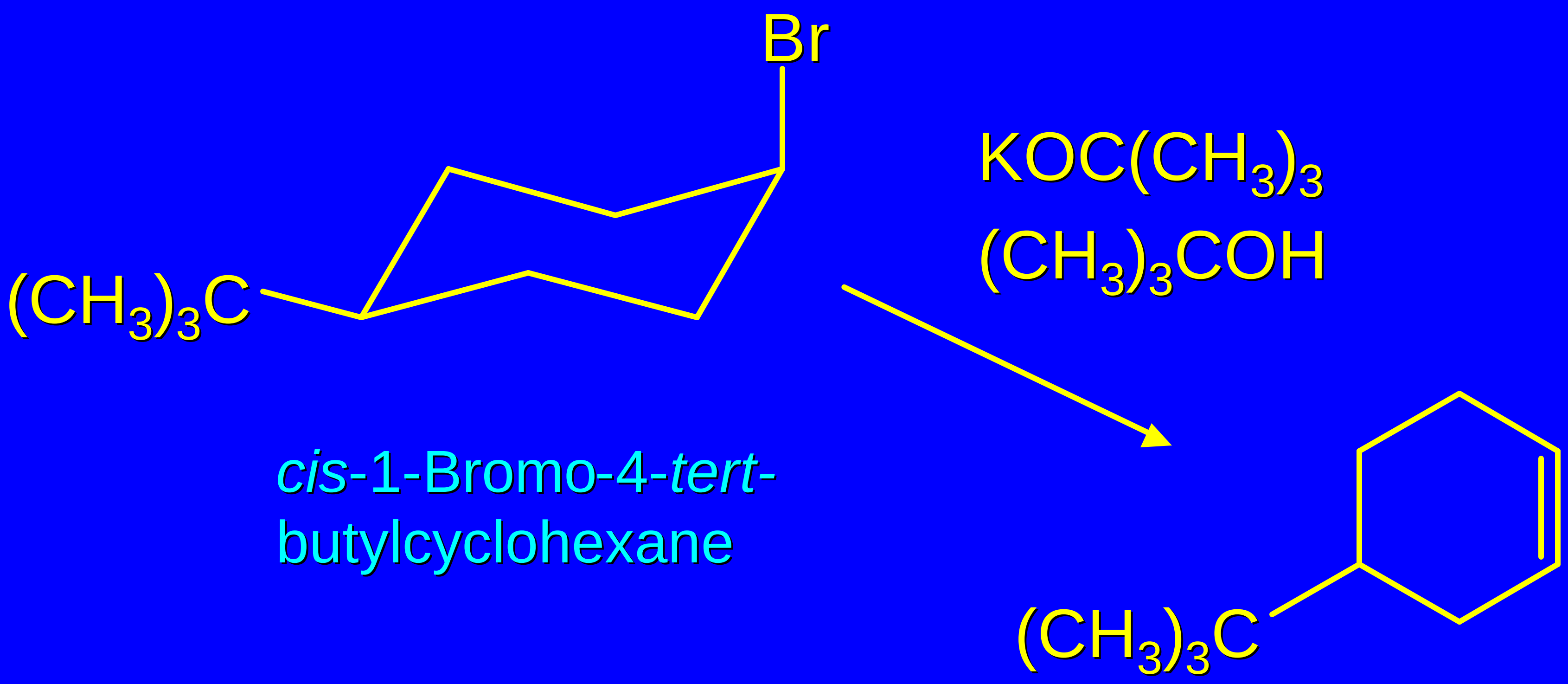
Products

5.16

Anti Elimination in E2 Reactions

Stereoelectronic Effects

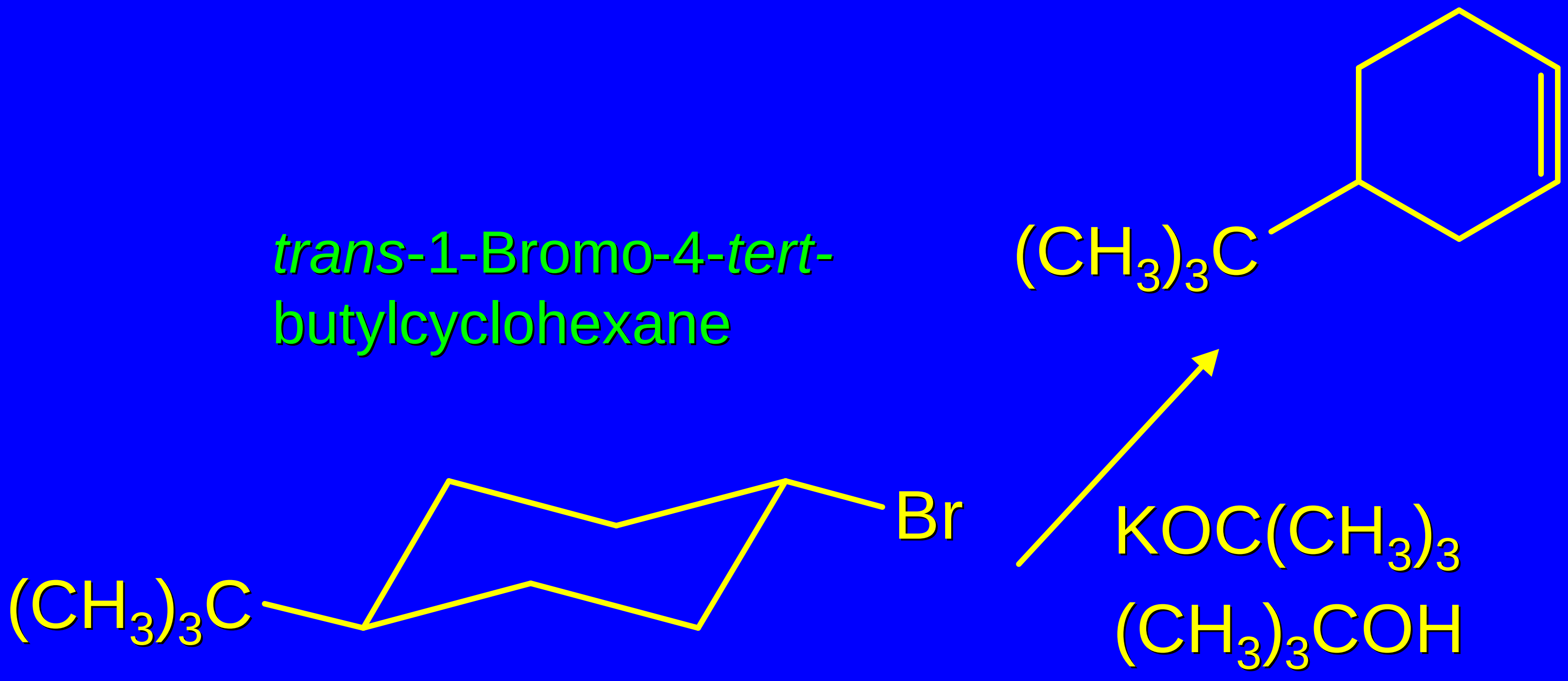
Stereoelectronic effect



$KOC(CH_3)_3$
$(CH_3)_3COH$

cis-1-Bromo-4-*tert*-butylcyclohexane

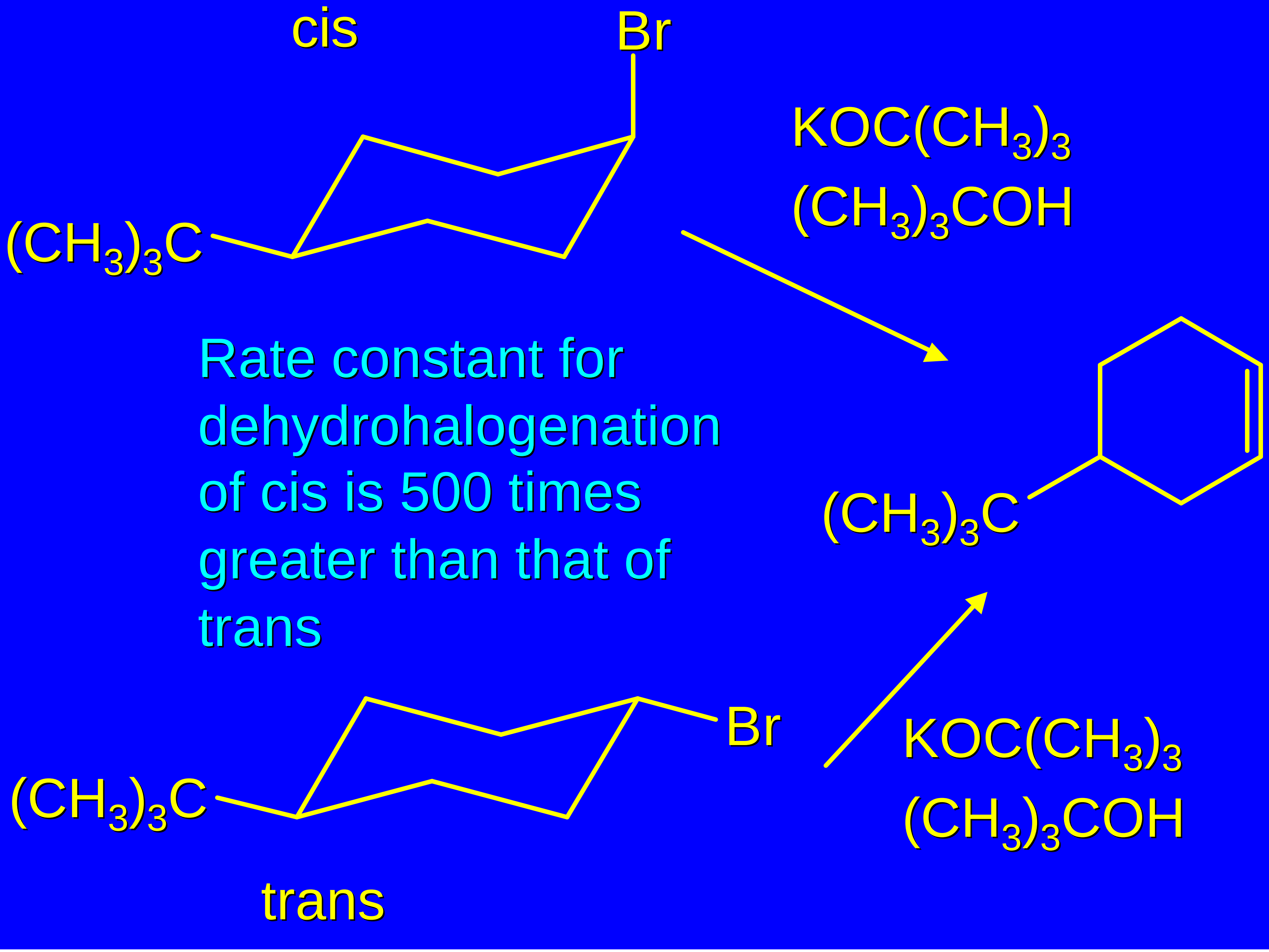
Stereoelectronic effect



trans-1-Bromo-4-*tert*-butylcyclohexane

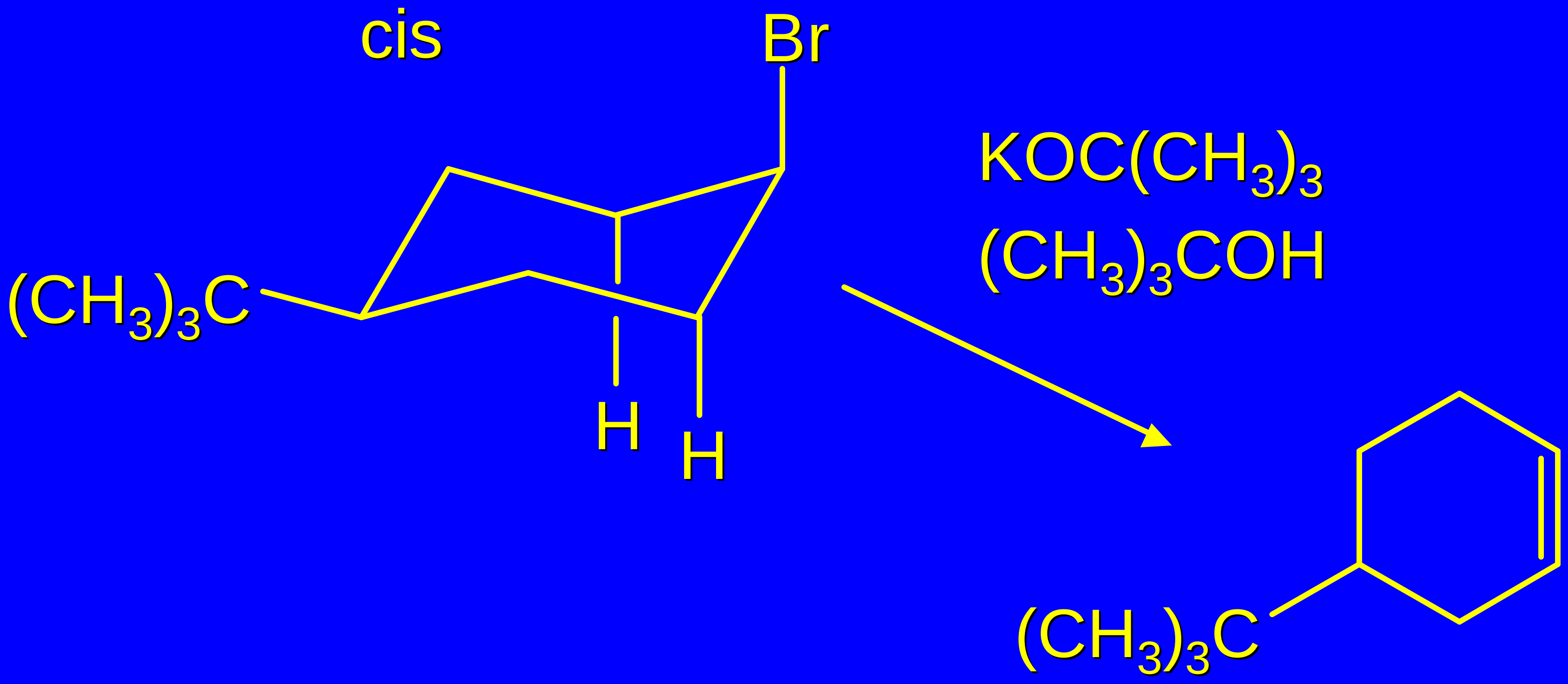
$KOC(CH_3)_3$
$(CH_3)_3COH$

Stereoelectronic effect



Rate constant for dehydrohalogenation of cis is 500 times greater than that of trans

Stereoelectronic effect

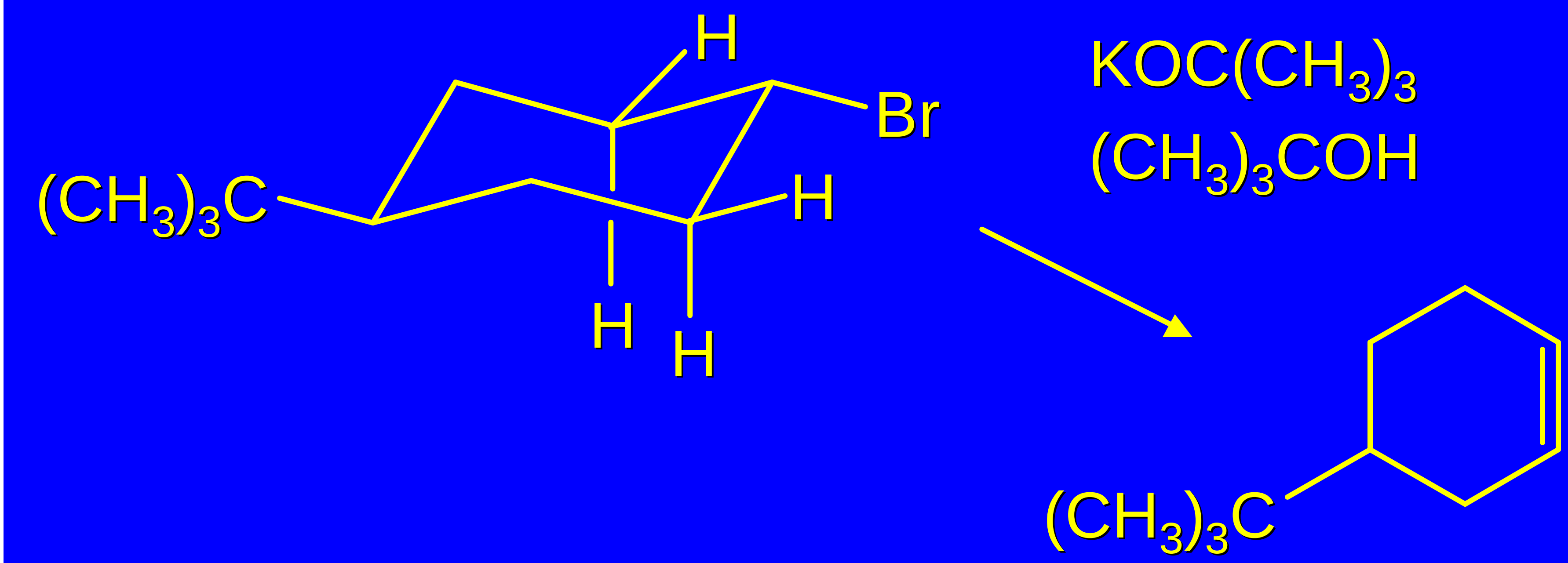


H that is removed by base must be anti periplanar to Br

Two anti periplanar H atoms in cis stereoisomer

Stereoelectronic effect

trans

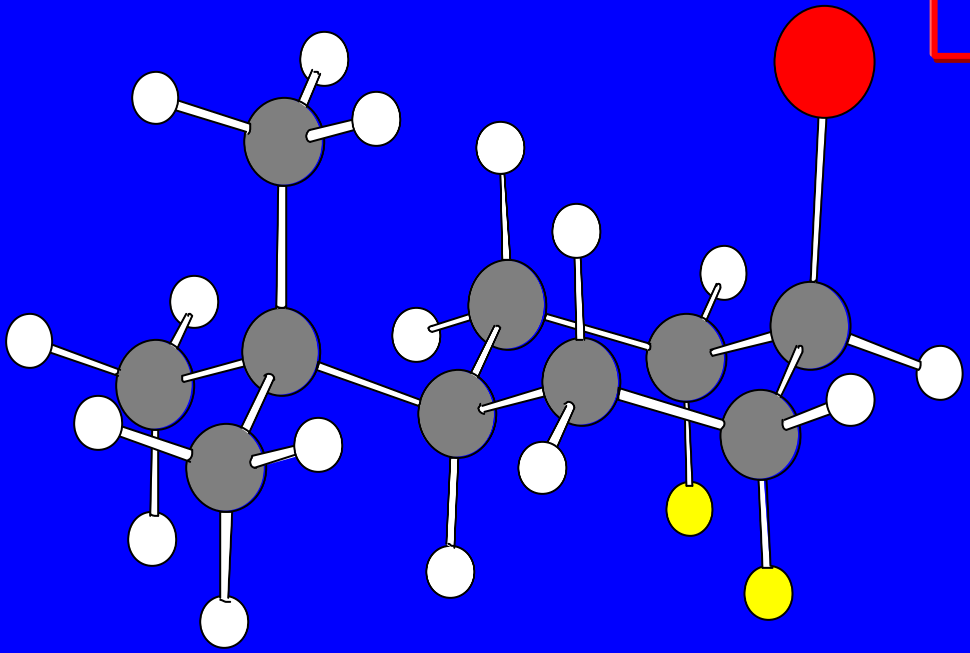


$KOC(CH_3)_3$
$(CH_3)_3COH$

H that is removed by base must be anti periplanar to Br

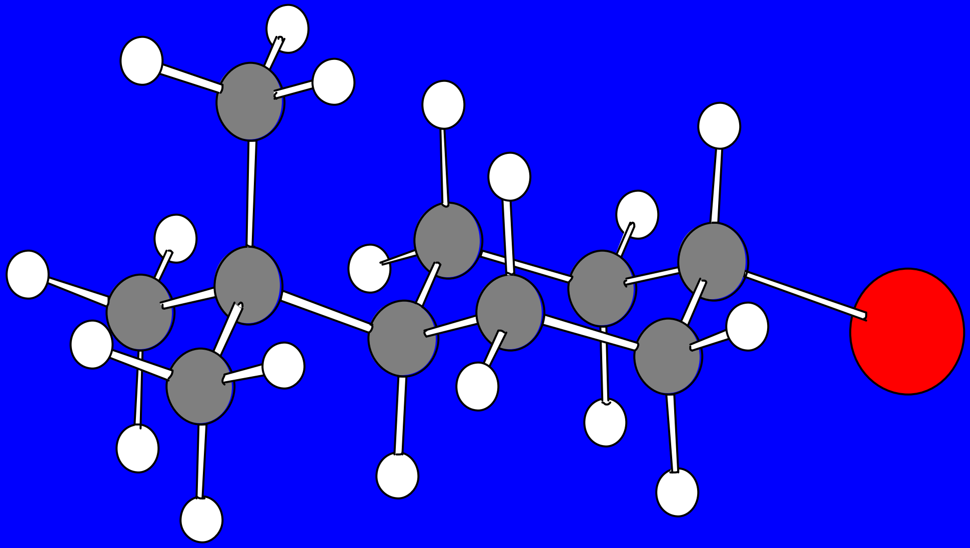
No anti periplanar H atoms in trans stereoisomer; all vicinal H atoms are gauche to Br

Stereoelectronic effect



cis

more reactive



trans

less reactive

Stereoelectronic effect

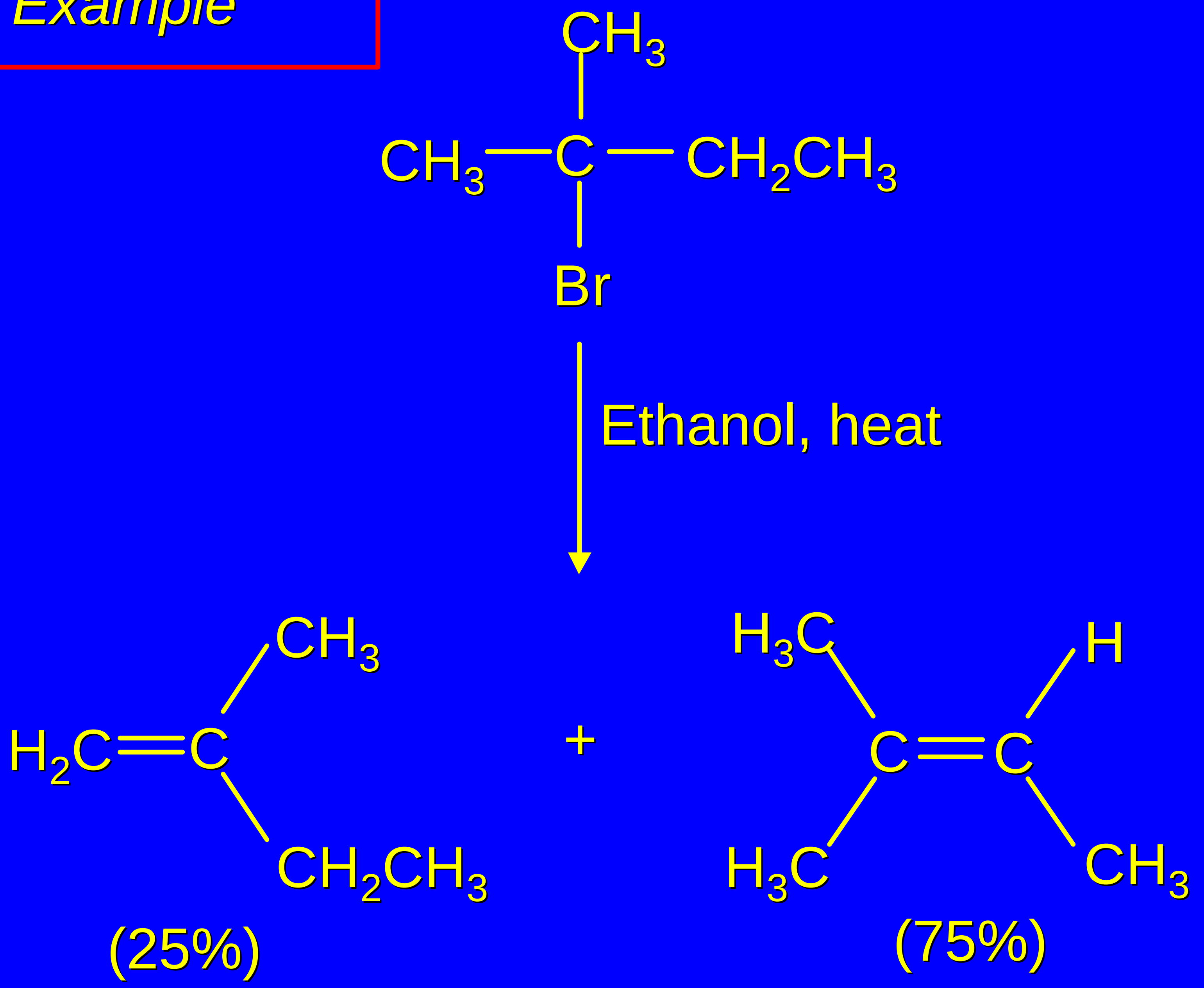
An effect on reactivity that has its origin in the spatial arrangement of orbitals or bonds is called a stereoelectronic effect.

The preference for an anti periplanar arrangement of H and Br in the transition state for E2 dehydrohalogenation is an example of a stereoelectronic effect.

5.17

A Different Mechanism for Alkyl Halide Elimination: The E1 Mechanism

Example



Ethanol, heat

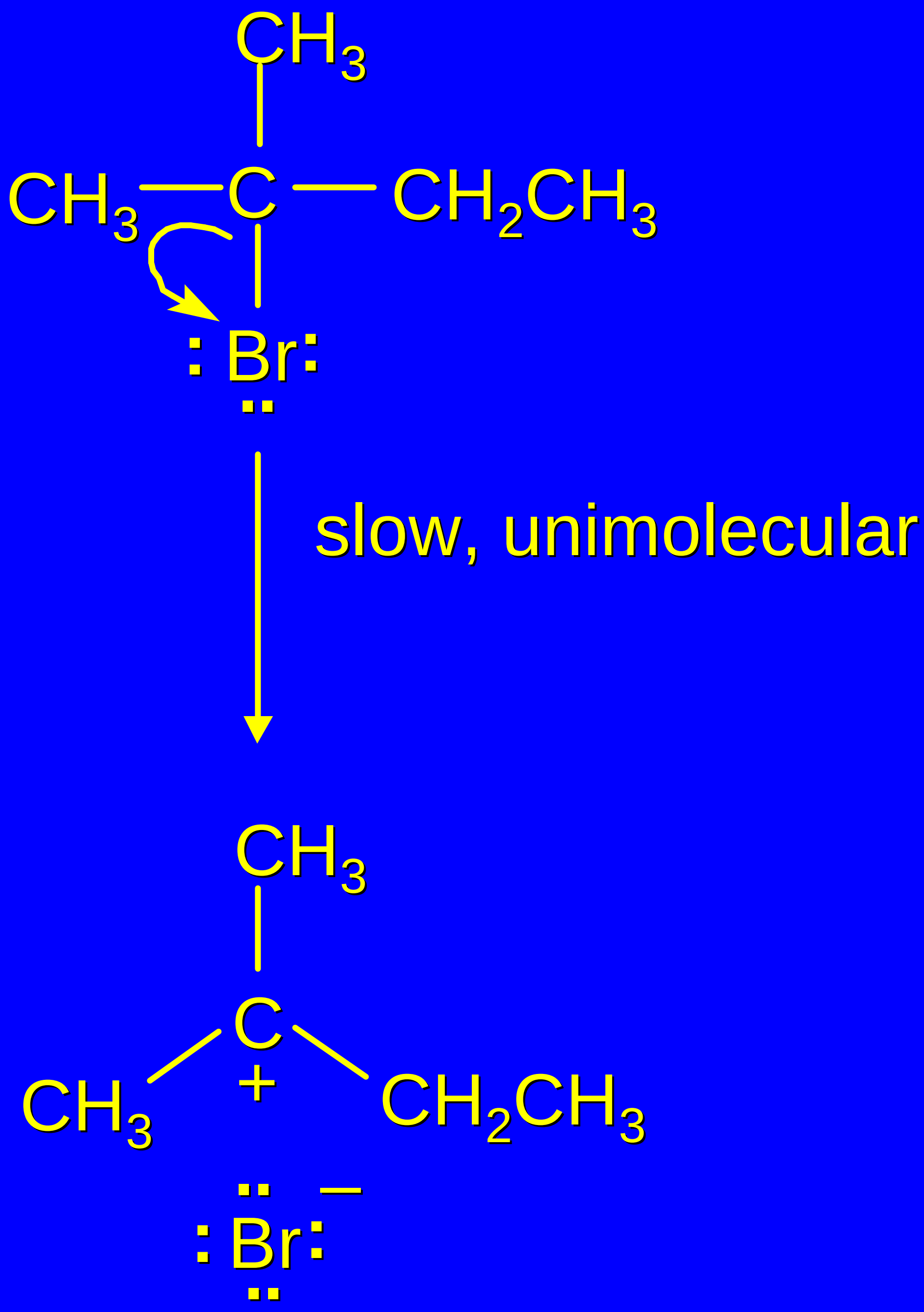
(25%)

(75%)

The E1 Mechanism

1. Alkyl halides can undergo elimination in absence of base.
2. Carbocation is intermediate
3. Rate-determining step is unimolecular ionization of alkyl halide.

Step 1



Step 2