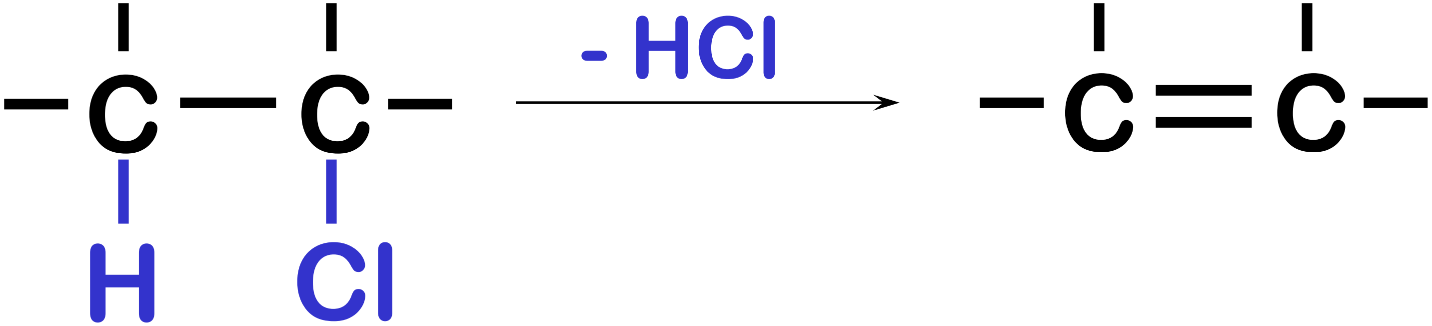
تفاعلات الإنتزاع
ELIMINATION REACTIONS

تفاعل الإنتزاع

ELIMINATION REACTIONS

تفاعل يتم فيه نزع جزيء صغير من المركب مثل (H_2O or HCl or Cl_2) وذلك خلال التفاعل ويتم تكوين الكين وسواء تم في خطوة واحدة او في خطوتين متتاليتين فإنه يمثل بالمعادلة العامة التالية .



TWO EXAMPLES FOLLOW

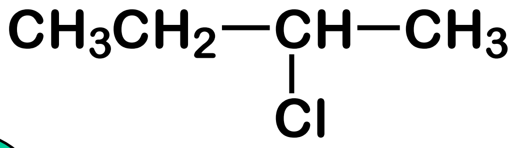
تفاعل الإنتزاع

مثالان

E2

هاليد الألكيل + قاعدة قوية بوجود تسخين	فقدان HCl
Alkyl halide + strong base and heat	**LOSS OF HCl**

$$CH_3CH_2CH_2CH_2{-}Cl \xrightarrow[\Delta]{NaOH} CH_3CH_2{-}CH{=}CH_2$$



$$CH_3CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 \xrightarrow[\Delta]{NaOH} CH_3{-}CH{=}CH{-}CH_3$$

E1

Alcohol + strong acid and heat	**LOSS OF H_2O**

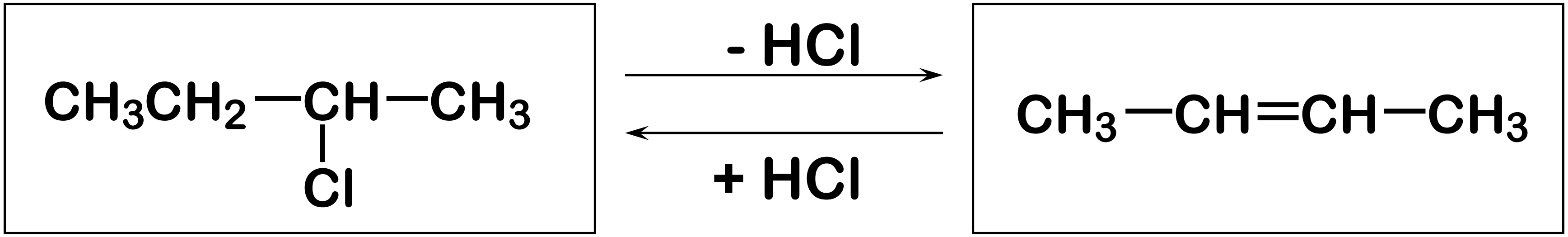
$$CH_3CH_2CH_2CH_2{-}OH \xrightarrow[\Delta]{H_2SO_4} CH_3CH_2{-}CH{=}CH_2$$

تفاعل الانتزاع عبارة عن معكوس تفاعل الإضافة

ظروف قاعدية + تسخين

basic conditions + heat

NaOH + heat



$$CH_3CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \;\underset{+\,HCl}{\overset{-\,HCl}{\rightleftarrows}}\; CH_3-CH=CH-CH_3$$

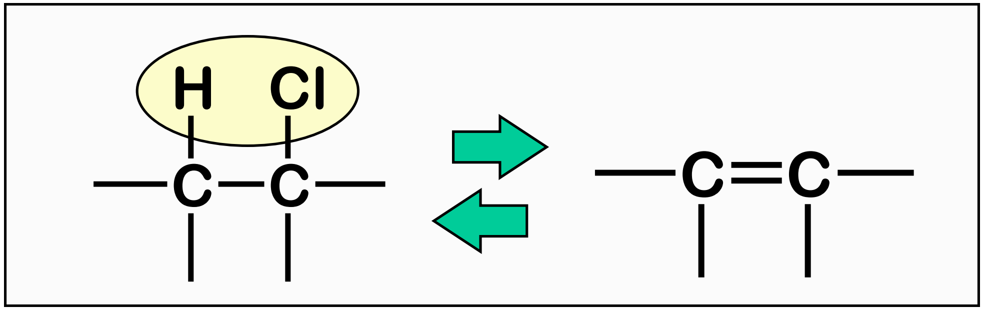
ALKYL HALIDE

ALKENE

conc. HCl

ظروف حمضية

acidic conditions



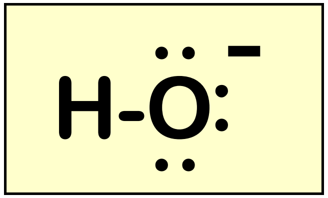
القاعدة القوية

STRONG BASES

ما هي القواعد القوية ؟

NaOH

sodium hydroxide هيدروكسيد الصوديوم

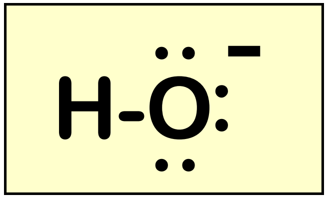


يستخدم وع الماء كمذيب ولكن معظم الهاليدات لاتذوب في الماء

$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2(g)$$

KOH

potassium hydroxide هيدروكسيد البوتاسيوم



يذوب فب الماء والميثانول والإثانول ومعظم الهاليدات تذوب
في الميثانول والإثانول

$$2\ K + 2\ H_2O \longrightarrow 2\ KOH + H_2(g)$$

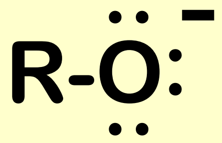
ما هي القواعد القوية ؟

NaOR sodium alkoxides صوديوم الكوكسيد

دائما ما يستخدم مع الكحول المشتق منه كمذيب ومعظم الهاليدات تذوب فيه

$$2\ Na + 2\ ROH \longrightarrow 2\ NaOR + H_2(g)$$

examples:



$$R\text{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$$

Stronger bases than hydroxides ….. why?

sodium methoxide

$NaOCH_3$ (NaOMe)

sodium ethoxide

$NaOCH_2CH_3$ (NaOEt)

sodium t-butoxide

$NaOC(CH_3)_3$ (NaOtBu)

ما هي القواعد القوية ؟

$NaNH_2$ sodium amide صوديوم اميد

دائما ما يستخدم مع سائل الأمونيا كمذيب

$$:\ddot{N}H_2^{-}$$

$$2\,Na \;+\; 2\,NH_3 \xrightarrow[\substack{NH_3\,(liq)\\ -33\ ^{o}C}]{FeCl_3} 2\,NaNH_2 \;+\; H_2$$

A stronger base than the hydroxides or the alkoxides …. why?

NH_3

A gas at room temp

ammonia

bp -33.4 °C ← liquifies

mp -77.7 °C ← solidifies

القواعد القوية

والتي تستخدم في تفاعلات الإنتزاع

Base	*Solvents Allowed*
NaOH	water
KOH	water, MeOH, EtOH
NaOR	ROH (same R group)
$NaNH_2$	NH_3 (liq) -33° C

Halides (RX) are not soluble in water, but are soluble in most alcohols, therefore, KOH or sodium alkoxides in alcohol are most often used.

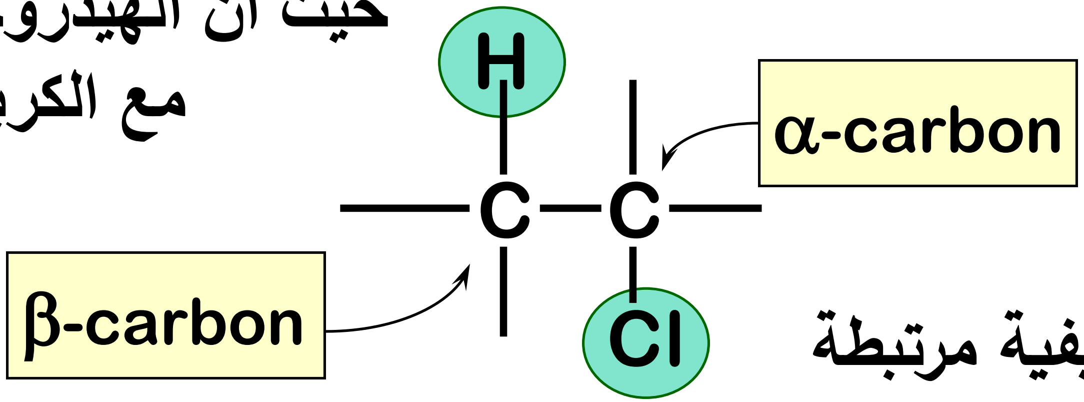
تعلم هذا جيدا فإنها معادلة تفاعل ازالة هاليد الهيدروجين

هاليد الكيل + قاعدة قوية + تسخين

E2 اختصار يدل على نوع تفاعل

هذا التفاعل يسمى انتزاع من ذرة الكربون بيتا - β

حيث ان الهيدروجين بيتا مرتبط
مع الكربون بيتا



المجموعة الوظيفية مرتبطة
مع ذرة الكربون الفا

وبما ان الهيدروجدين بيتا تنتزع فإن التفاعل يسمى بانتزاع بيتا

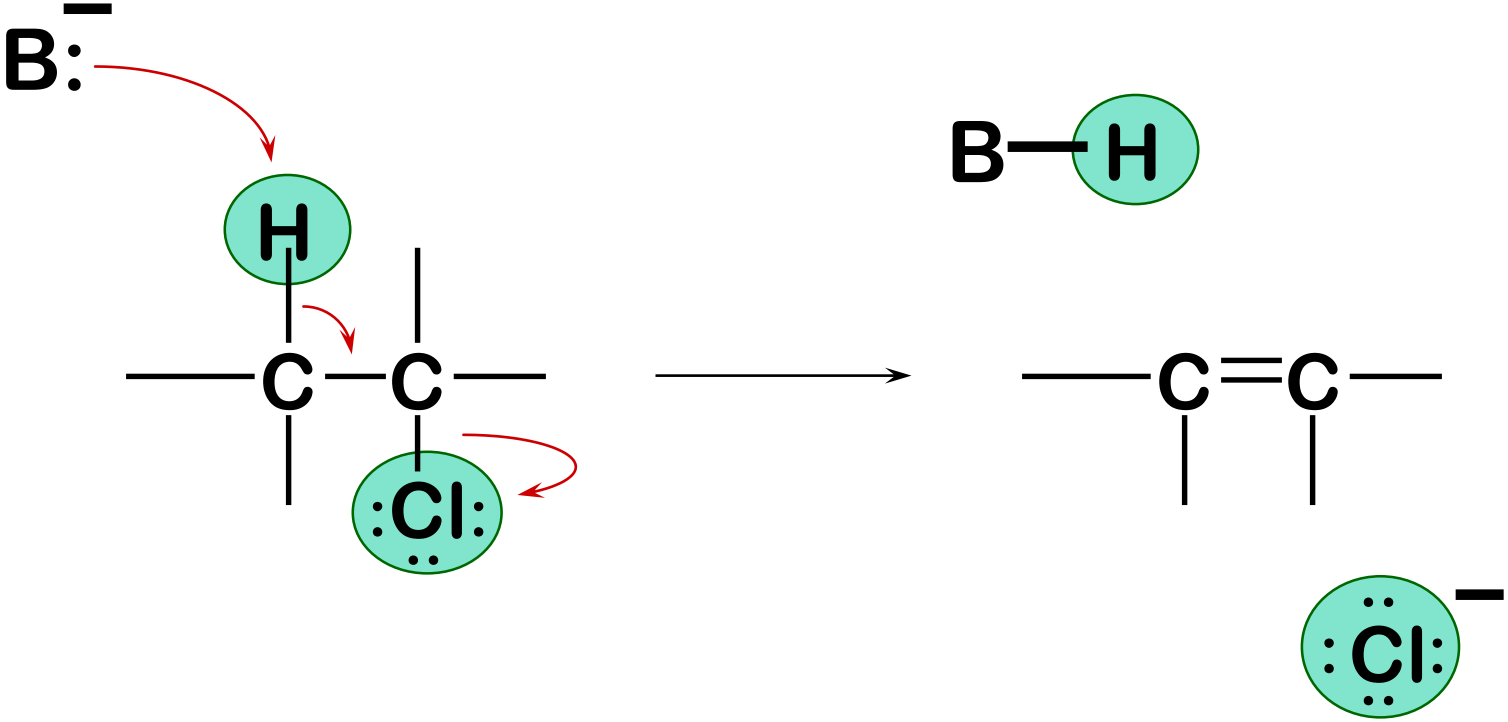
β-elimination.

مادة التفاعل = قاعدة قوية

Reagent = a strong base

ميكانيكية التفاعل

القاعدة تأخذ هيدروجين بيتا أولا



(E2)= قاعدة قوية + هاليد الكيل

ALKYL HALIDE + STRONG BASE (E2)

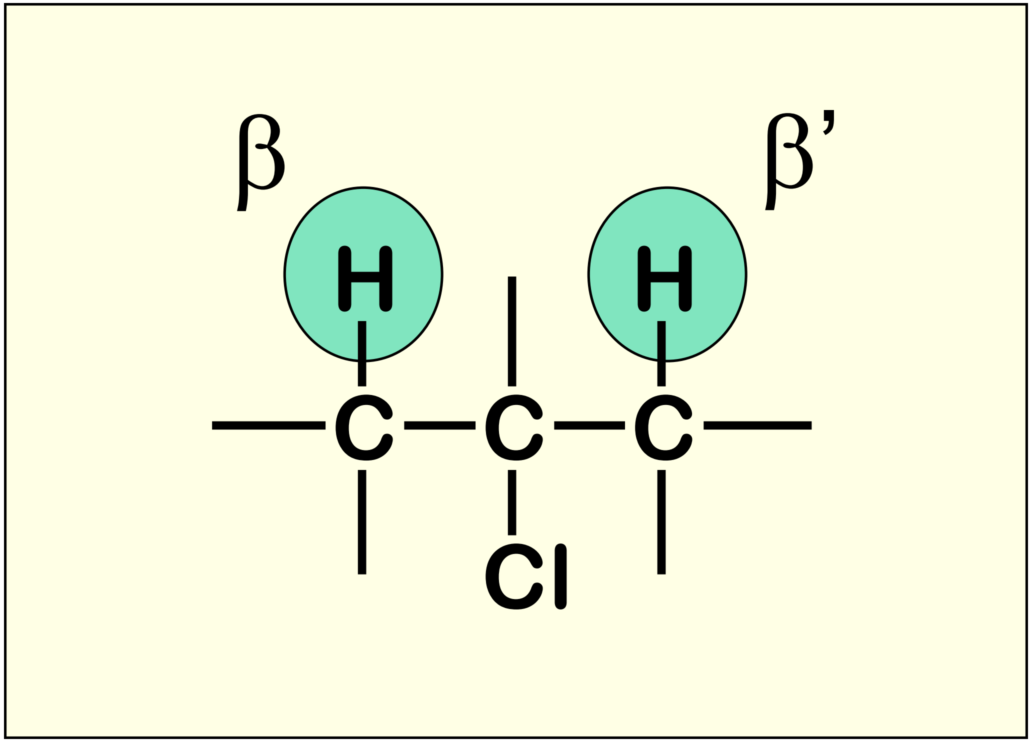
الاختيارية البنائية

REGIOSELECTIVITY

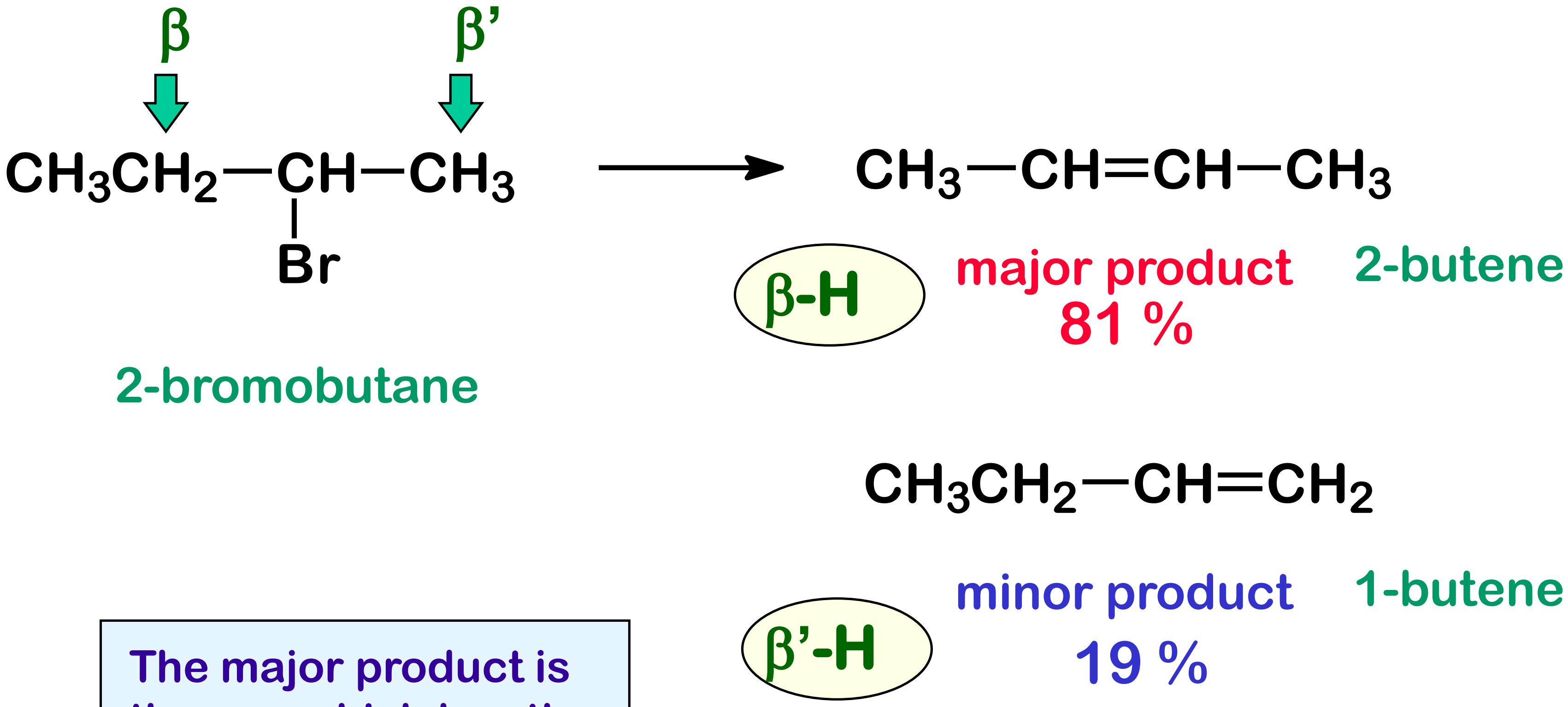
ماذا يحدث في حالة تواجد ذرتين من الهيدروجين على الموقع بيتا ؟

أي منهما سوف تنتزع ؟

Which one do we lose ?



الانتزاع يعتبر ذو توجه انتقائي .



$$CH_3CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \longrightarrow CH_3-CH{=}CH-CH_3$$

2-bromobutane

β-H major product 81 % 2-butene

$$CH_3CH_2-CH{=}CH_2$$

β’-H minor product 19 % 1-butene

The major product is the one which has the lowest energy.

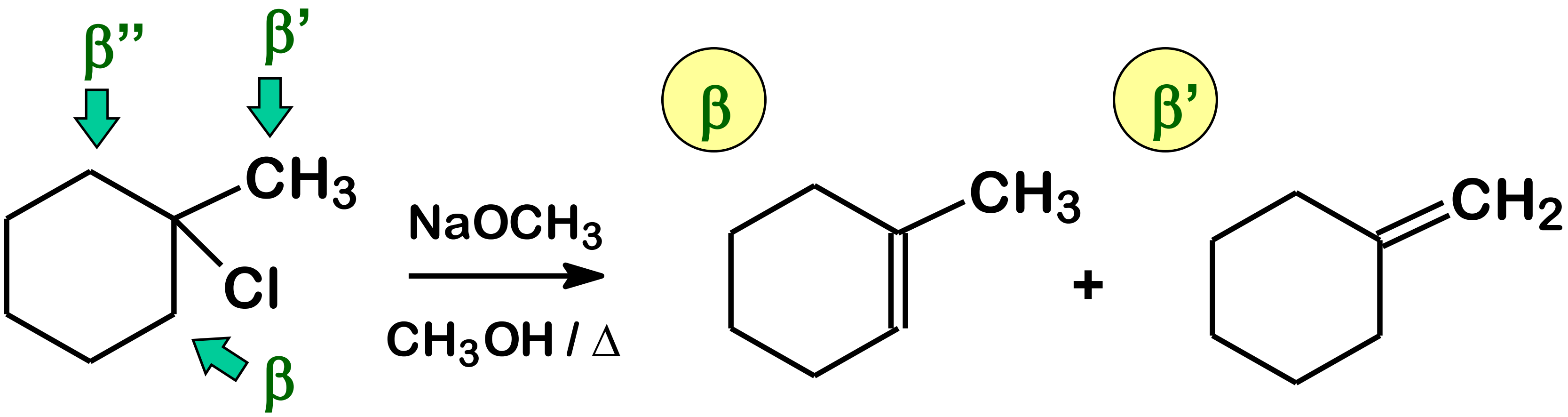
See the next slide.

اذا كان هناك اكثر من موقع في التوجه الإنتقائي

1-chloro-1-methylcyclohexane

methylenecyclohexane

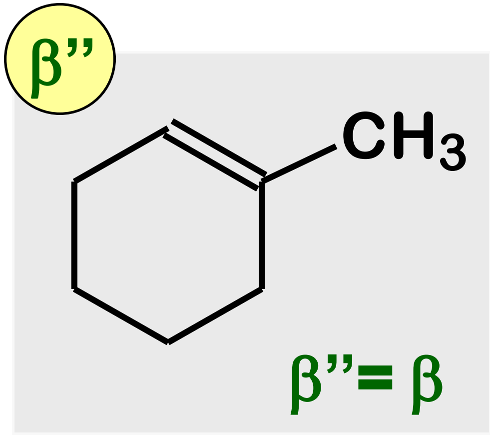
1-methylcyclohexene



major product

minor product

three possibilities
to lose β-hydrogens

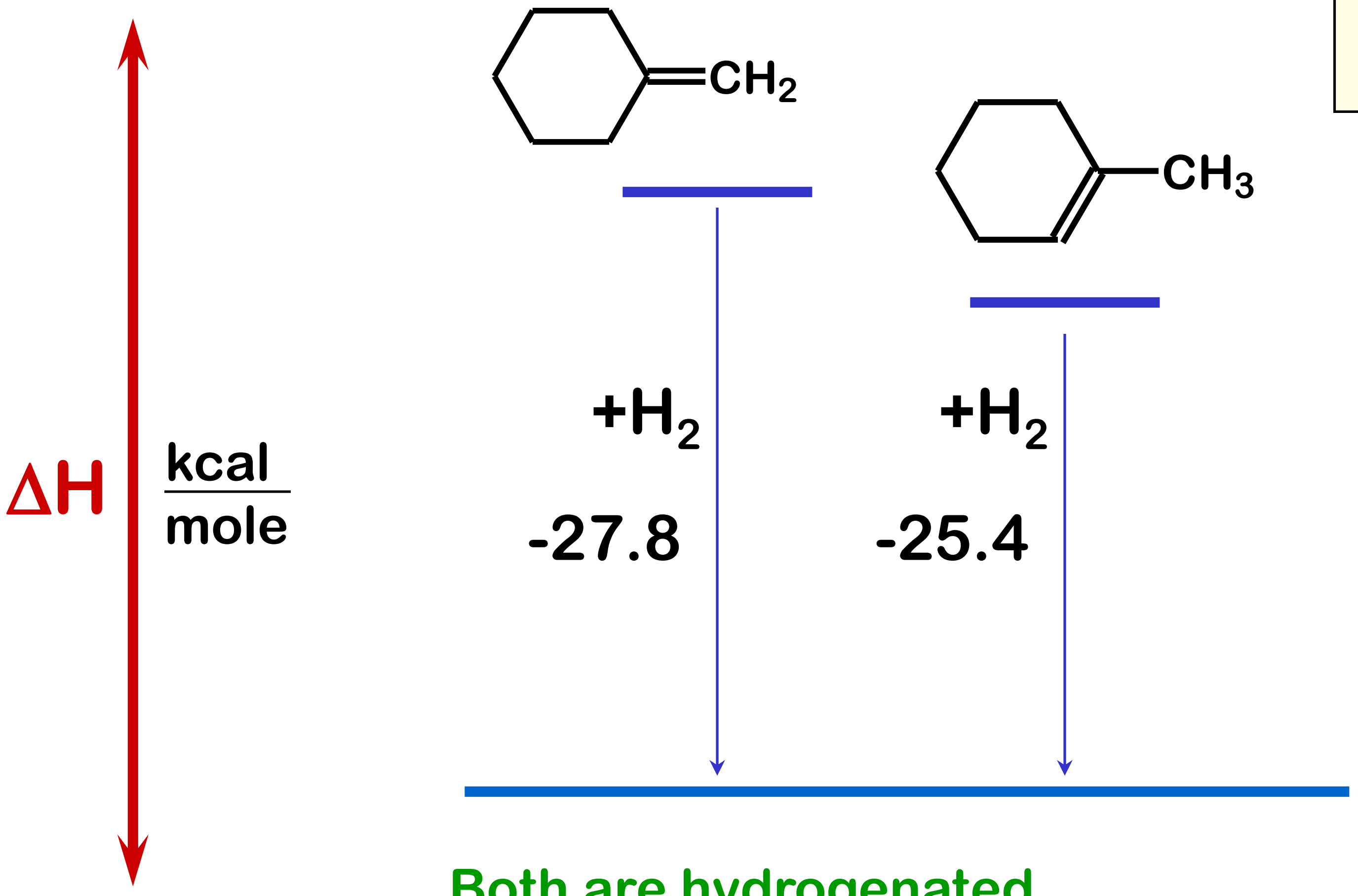


1-methylcyclohexene

identical to
β-product

METHYLCYCLOHEXENE ISOMERS

RECALL

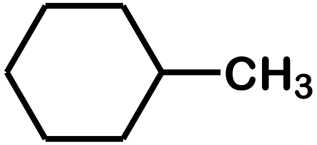


ΔH $\frac{\text{kcal}}{\text{mole}}$

$+H_2$ -27.8

$+H_2$ -25.4

Both are hydrogenated to the same product therefore their energies may be compared.



methylcyclohexane

Zaitsev

Tsayseff

etc.

قاعدة سيتزيف
SAYTZEV RULE

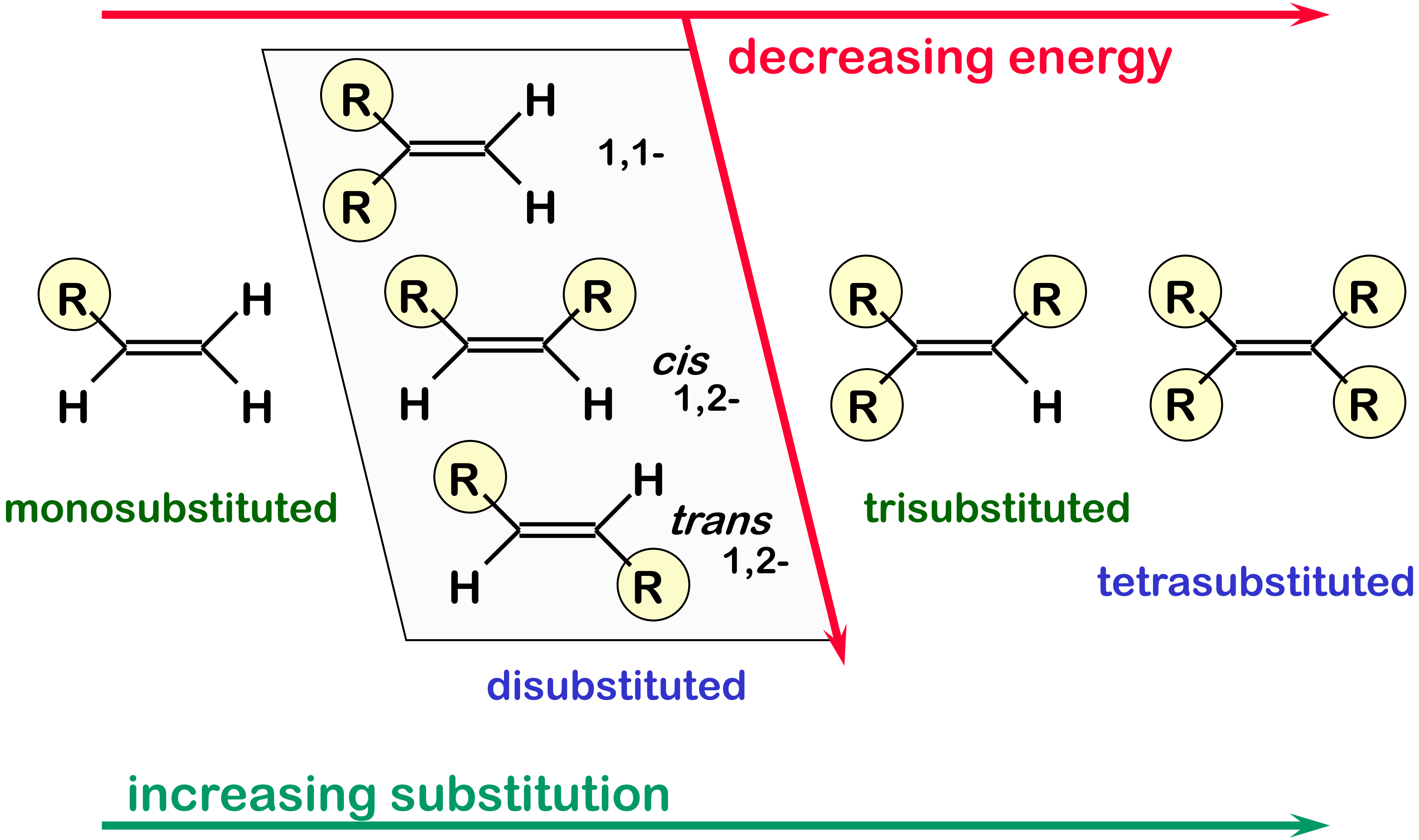
التفاعل ينتج الكين حيث يحتوي اكبر عدد من مجموعات الألكيل كبدائل على الرابطة الثنائية

The reaction gives the most highly-substituted (lowest energy) alkene as the major product.

متشكلات الألكينات

Different positions of the double bond.

المتشاكل الأكثر في مجموعات الألكيل على الرابطة الثنائية هو الأكثر استقرارا



decreasing energy

monosubstituted

disubstituted

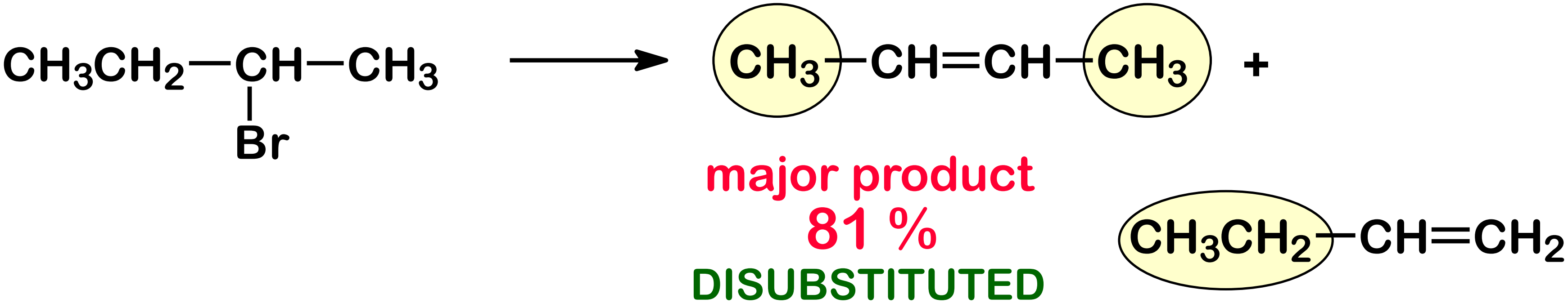
trisubstituted

tetrasubstituted

increasing substitution

تطبيقات قاعدة سيتزيف

2-bromobutane

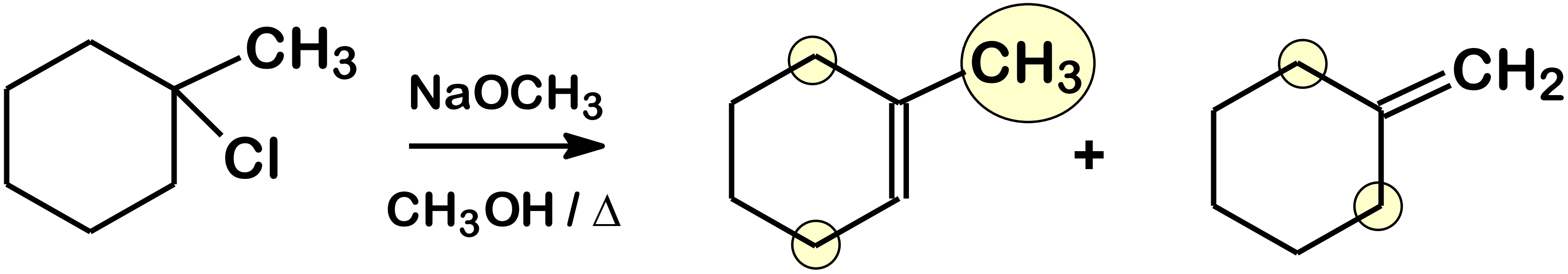


$$CH_3CH_2-\underset{Br}{\underset{|}{CH}}-CH_3 \longrightarrow CH_3-CH{=}CH-CH_3 + CH_3CH_2-CH{=}CH_2$$

major product
81 %
DISUBSTITUTED

minor product
19 %
MONOSUBSTITUTED

1-chloro-1-methylcyclohexane



major product

TRISUBSTITUTED

minor product

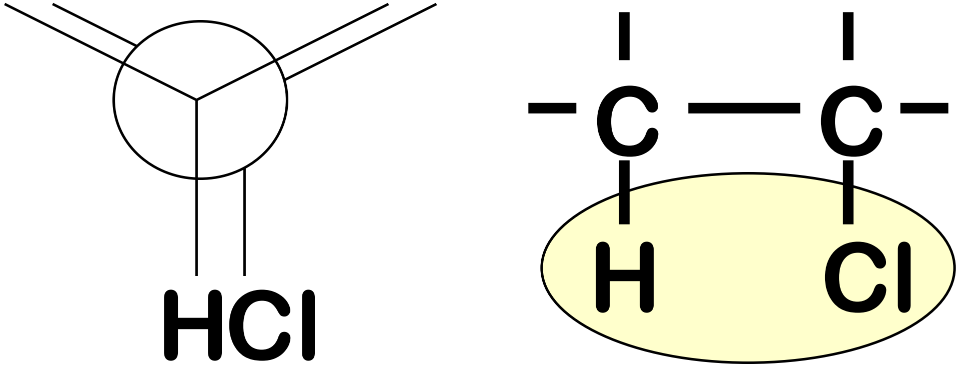
DISUBSTITUTED

ALKYL HALIDE + STRONG BASE (E2)

الكيمياء الفراغية للتفاعل

الكيمياء الفراغية

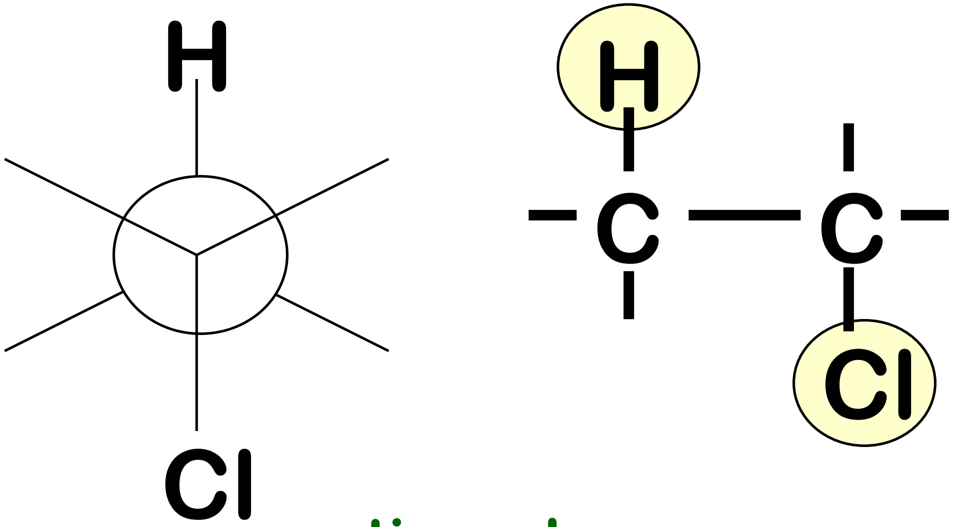
احتمالين قويين لإتمام الإنتزاع



انتزاع في نفس الاتجاه

syn elimination

غير شائع



anti-coplanar

انتزاع في اتجاهين متضادين

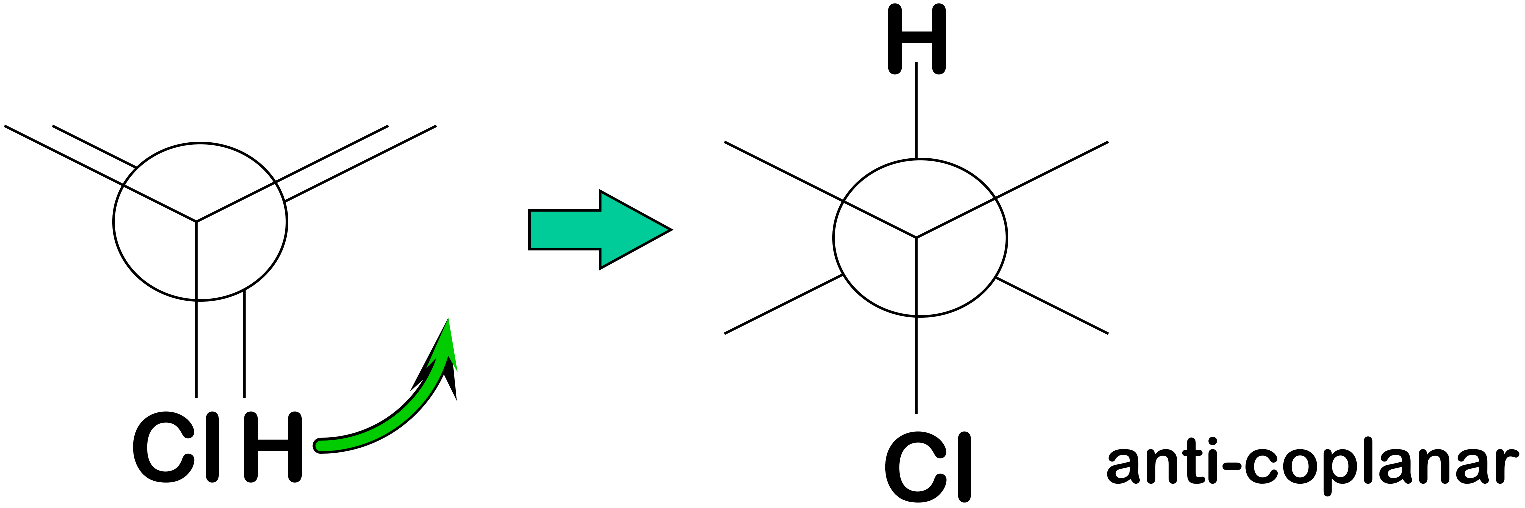
anti elimination

ملاحظ دائما

دراسة الكيمياء الفراغية

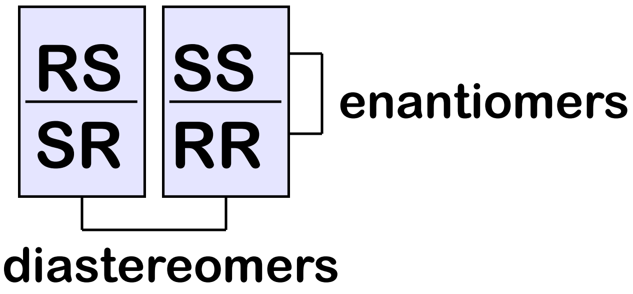
الهاليدات الغير حلقية

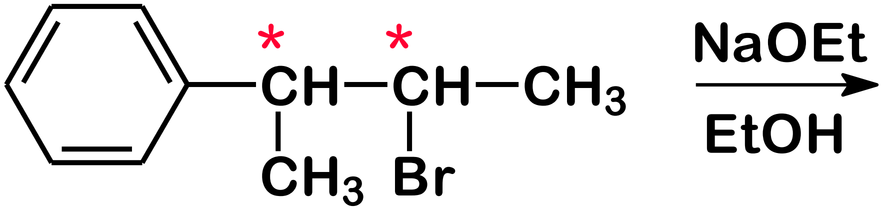
الهاليدات الألكيلية الغير حلقية ممكن ان تحتاج للدوران لإتمام التفاعل

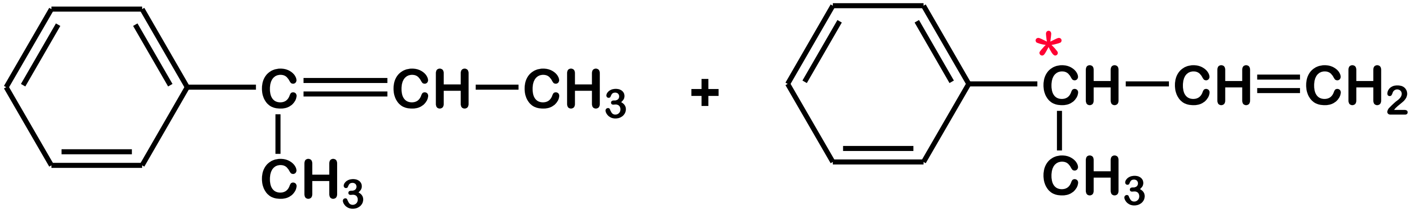


2-Bromo-3-phenylbutane

two stereocenters







Major Product

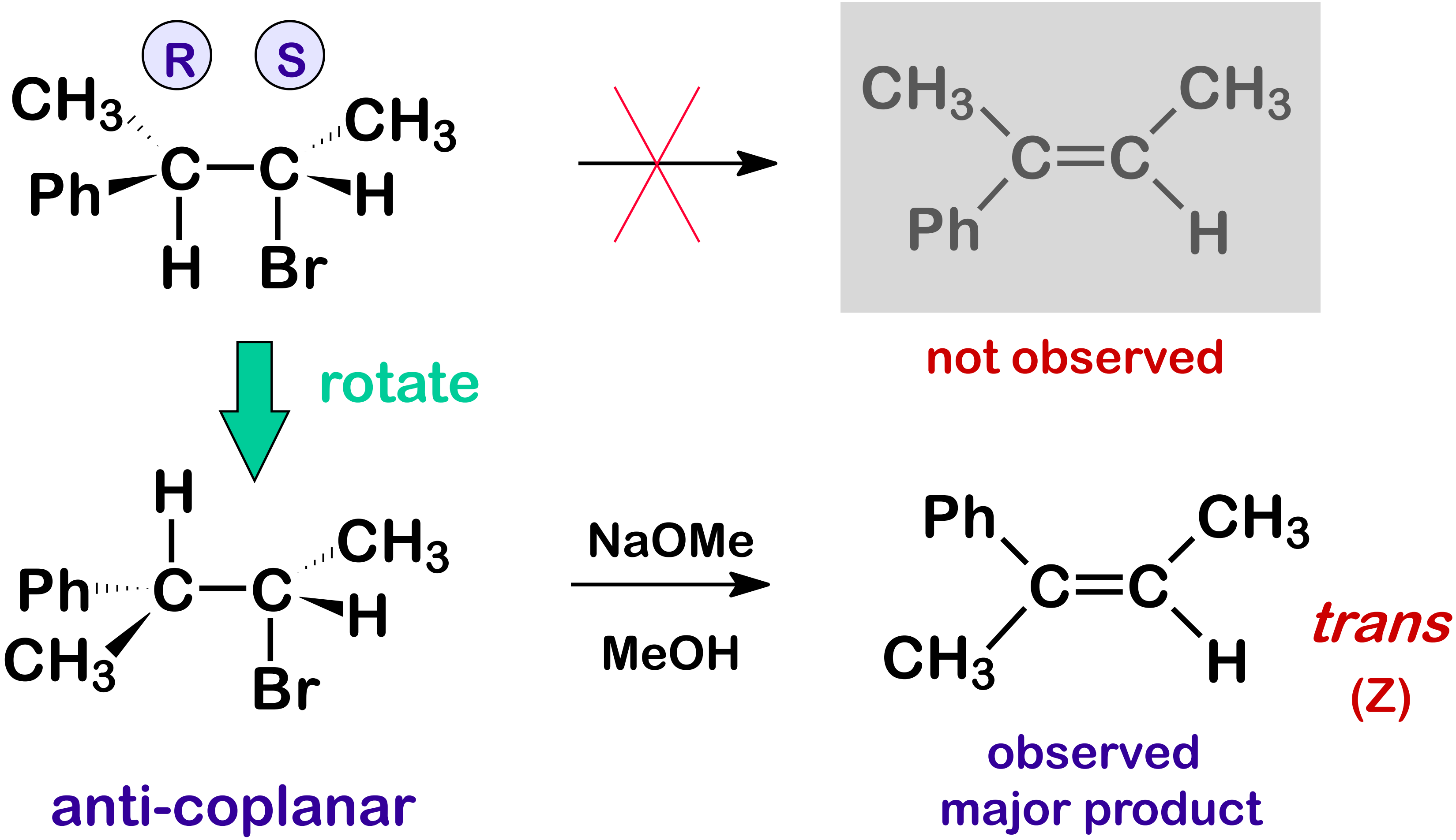
Zaitsev

Minor Product

cis or *trans*?

هل الكيمياء الفراغية مهمة ؟

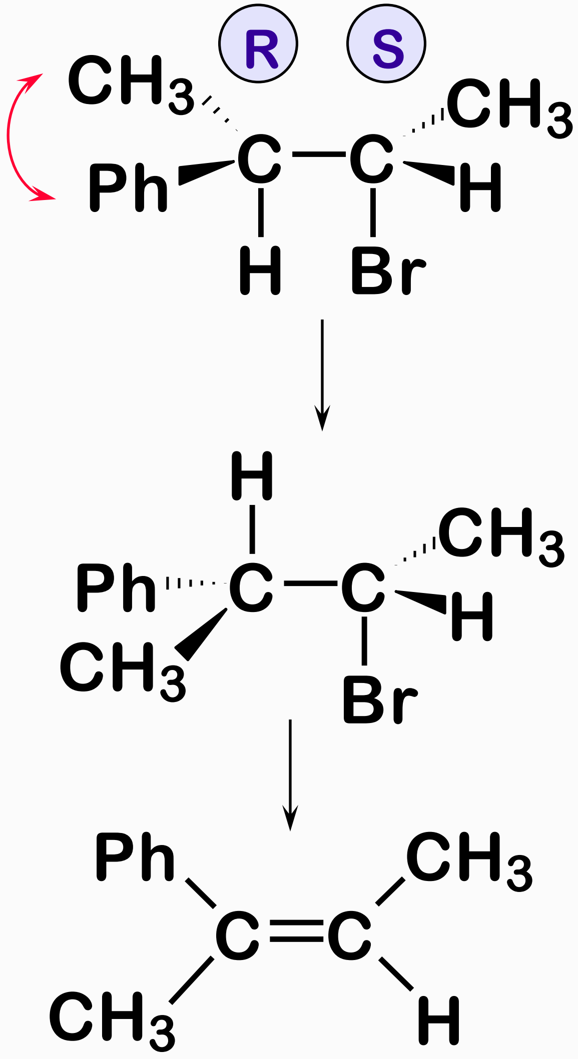
2S,3R-DIASTEREOMER



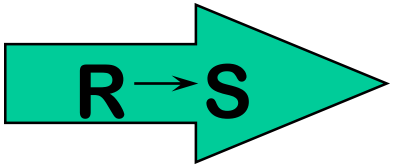
trans-2-phenyl-2-butene

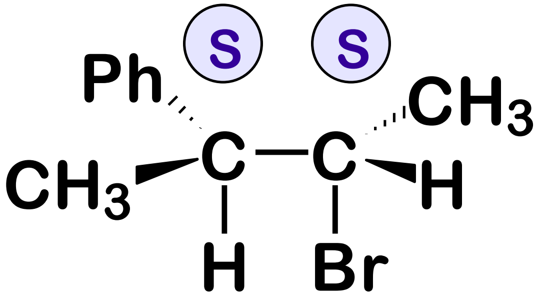
(plus some 1-butene due to β-H on the CH_3)

MAKING THE 2S,3S-DIASTEREOMER



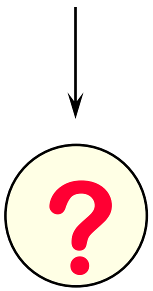
trans (Z)





make diastereomer

(change one stereocenter)

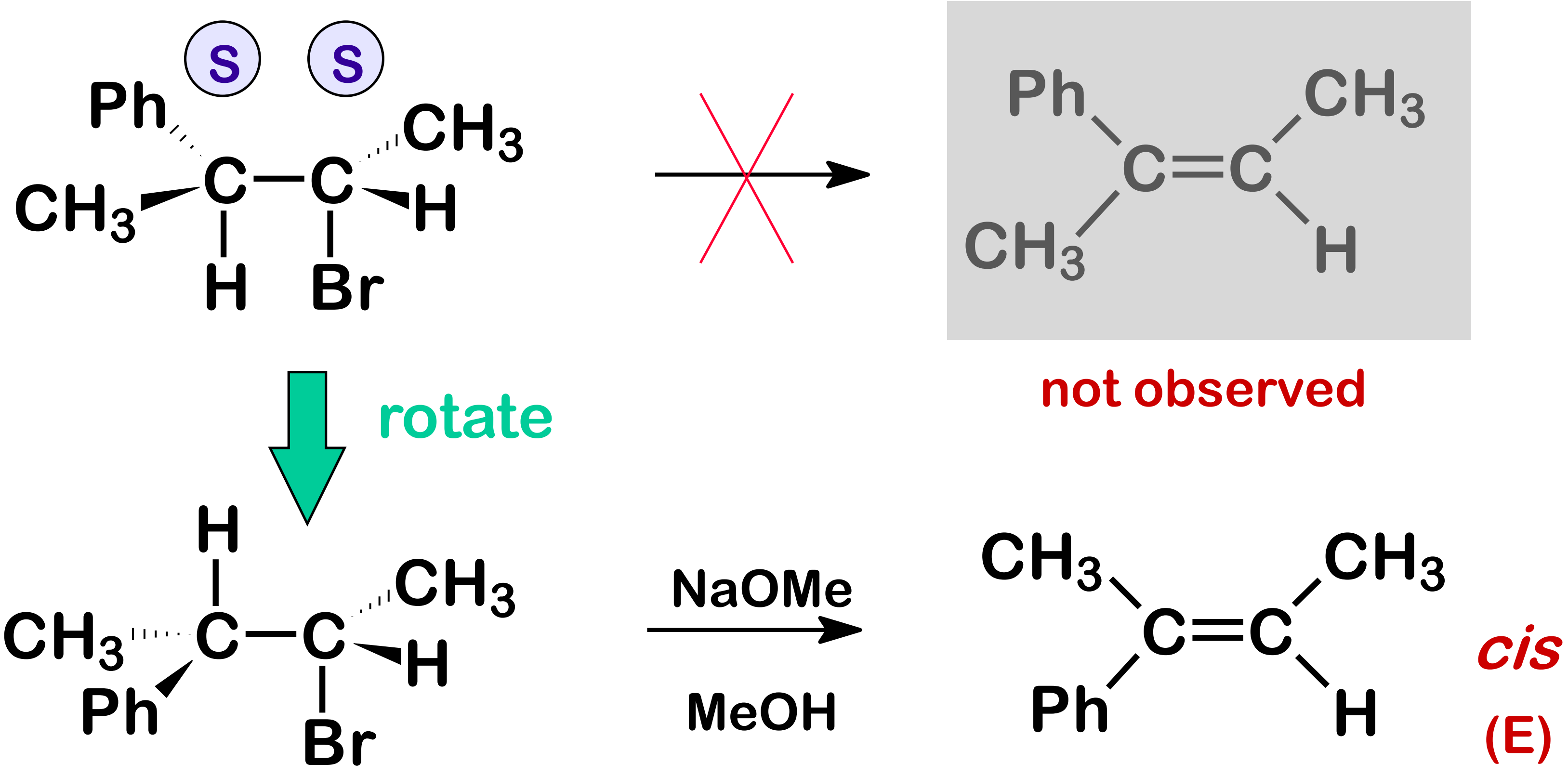


cis or trans?

WHAT DO YOU THINK?

Will the 2S,3S-diastereomer give the same product as its 2S,3R diastereomer?

2S,3S-DIASTEREOMER



anti-coplanar

observed
major product

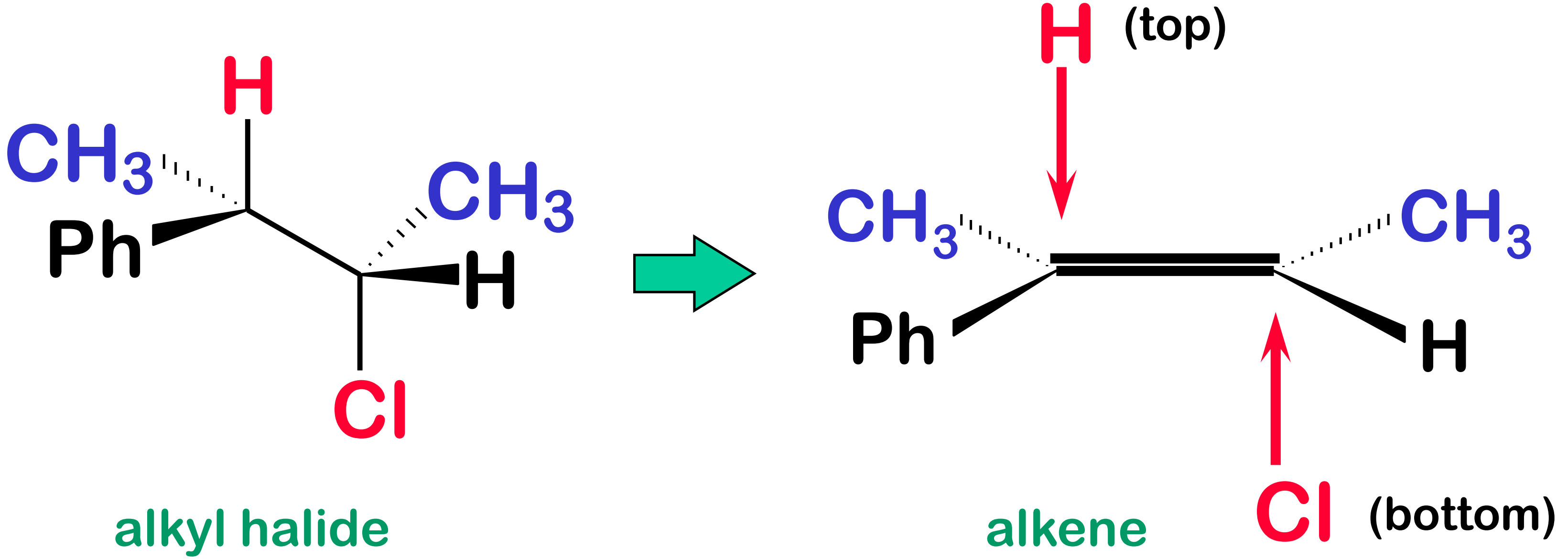
cis-2-phenyl-2-butene

(plus some 1-butene)

NO

A DIFFERENT PRODUCT IS
FORMED THAN WITH 2S,3R !

تحويل هاليدات الألكيل الى الكينات

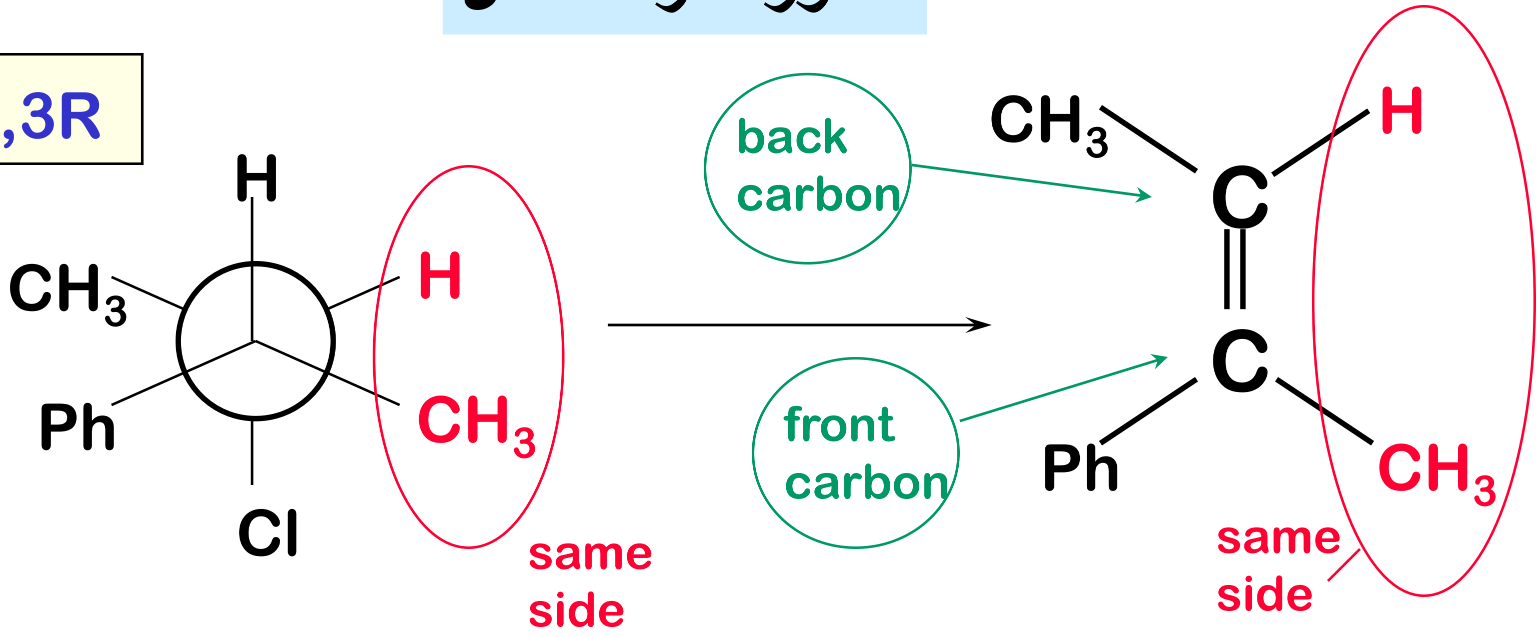


The methyl groups (blue) are in back in both structures.

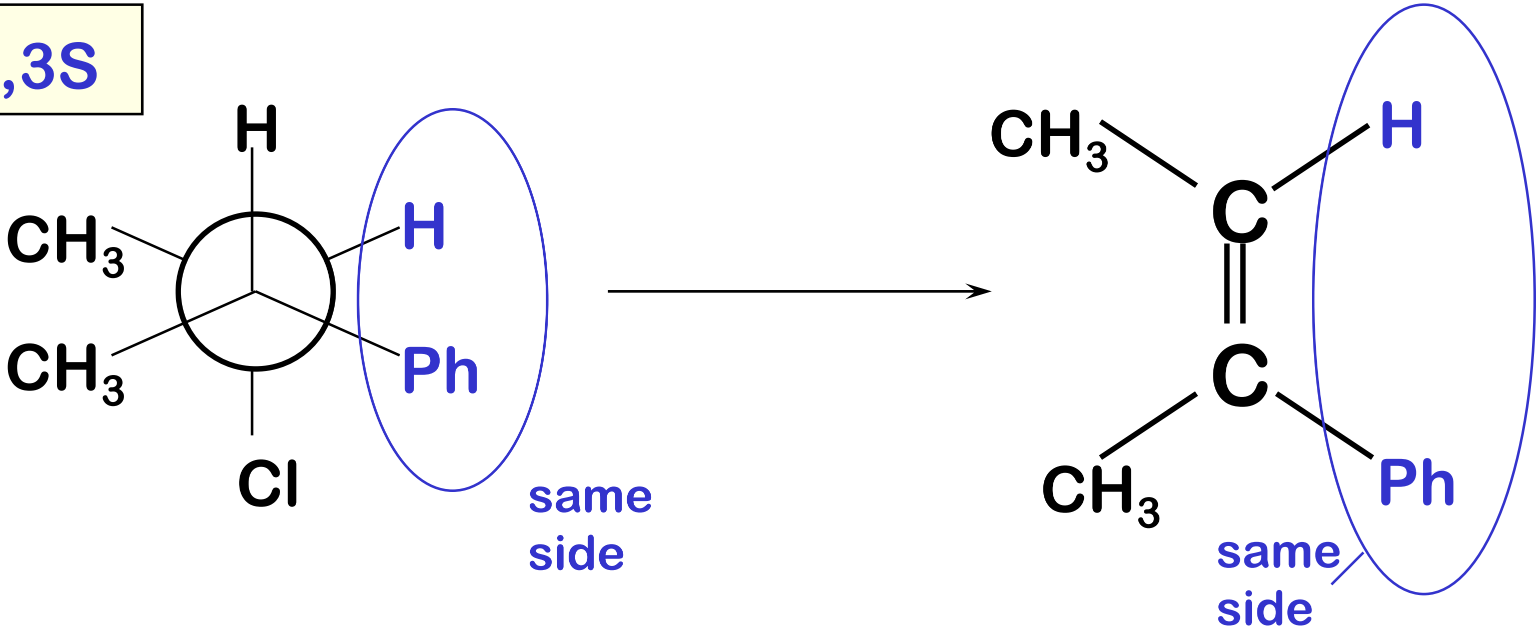
The phenyl and the hydrogen (black) are in front in both.

تصور اخر للتفاعل

2S,3R



2S,3S



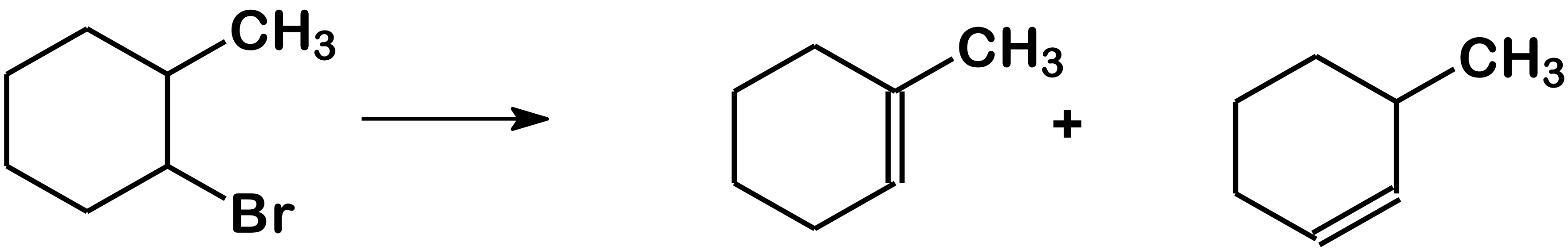
الهاليدات الحلقية الألكيلية

CYCLIC HALIDES

STEREOCHEMISTRY REARS ITS UGLY HEAD AGAIN !

1-Bromo-2-methylcyclohexane

The expected result (naïve) :



major product

Zaitsev

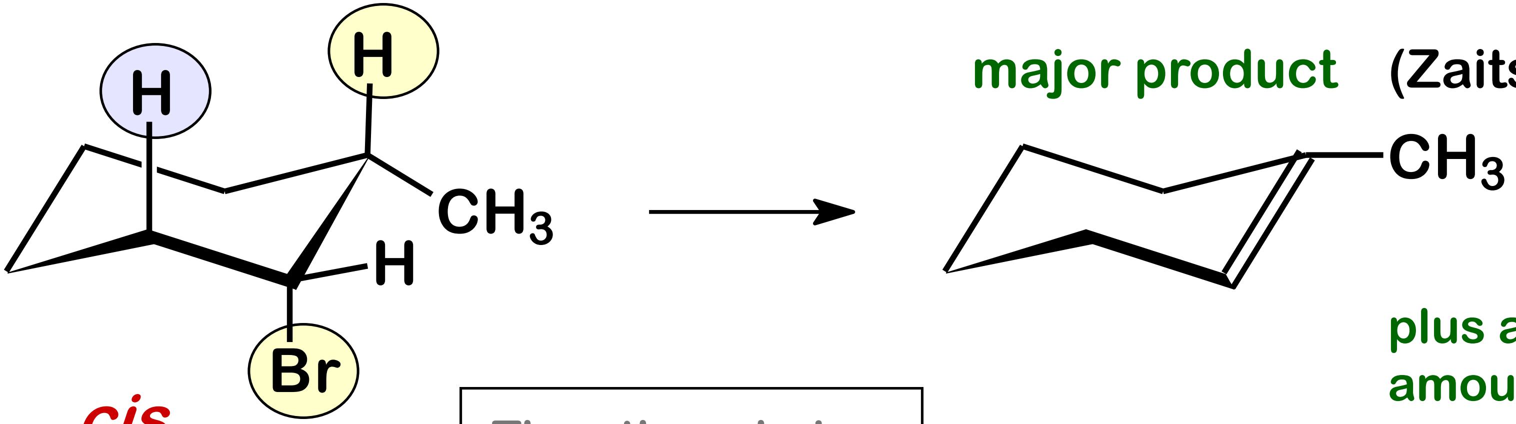
minor

drawn flat without stereochemistry

The result actually depends on the stereochemistry of the starting material (*cis* or *trans*).

THE *CIS* STEREOISOMER

The elimination needs to have H and Br anti-coplanar

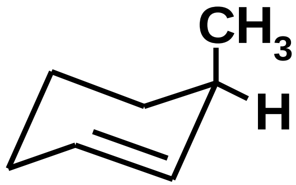


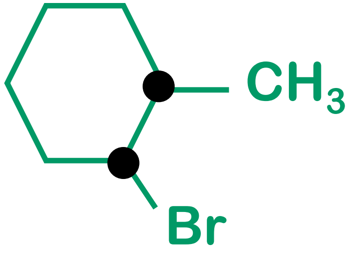
major product (Zaitsev)

cis

The other chair won't work. Why?

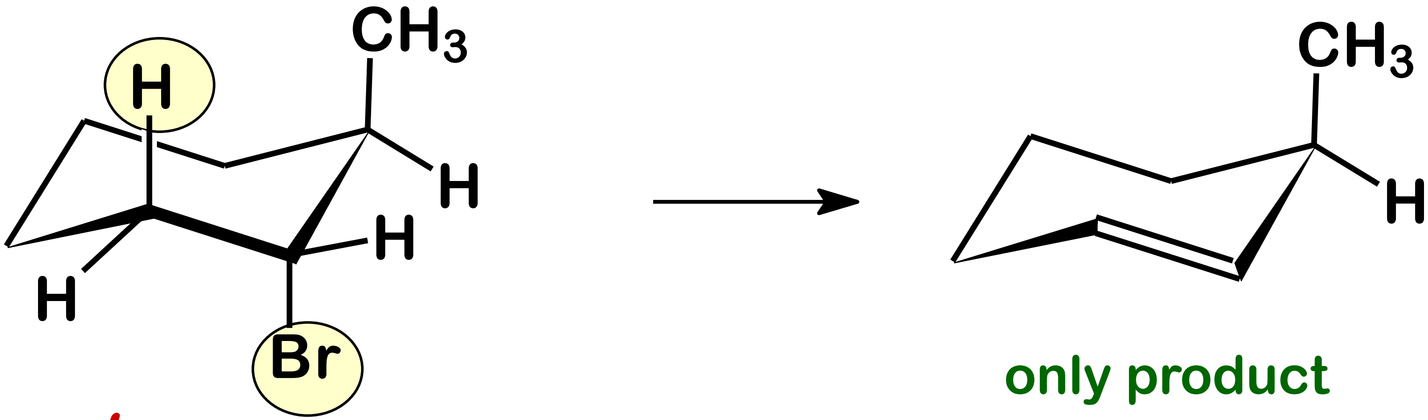
plus a small amount of





trans shown on next slide

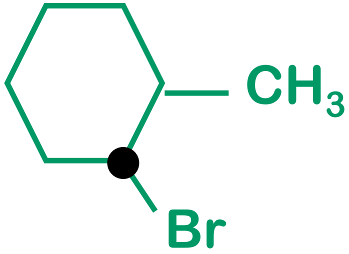
THE *TRANS* STEREOISOMER

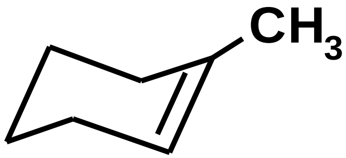


trans

only product

The other chair won’t work. Why?

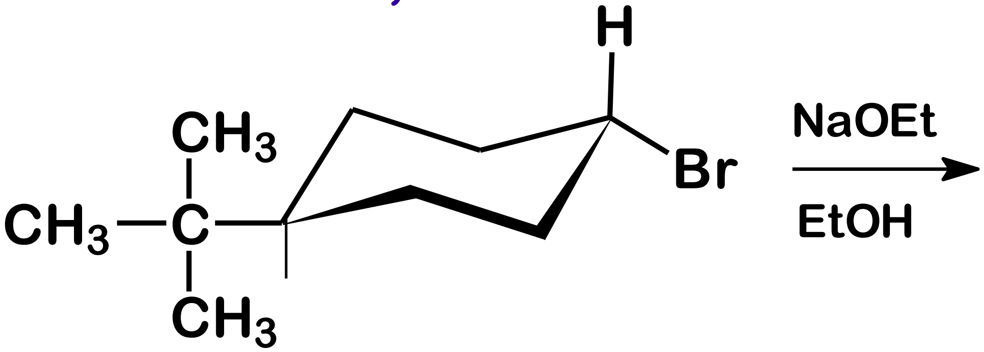




no methylcyclohexene is formed

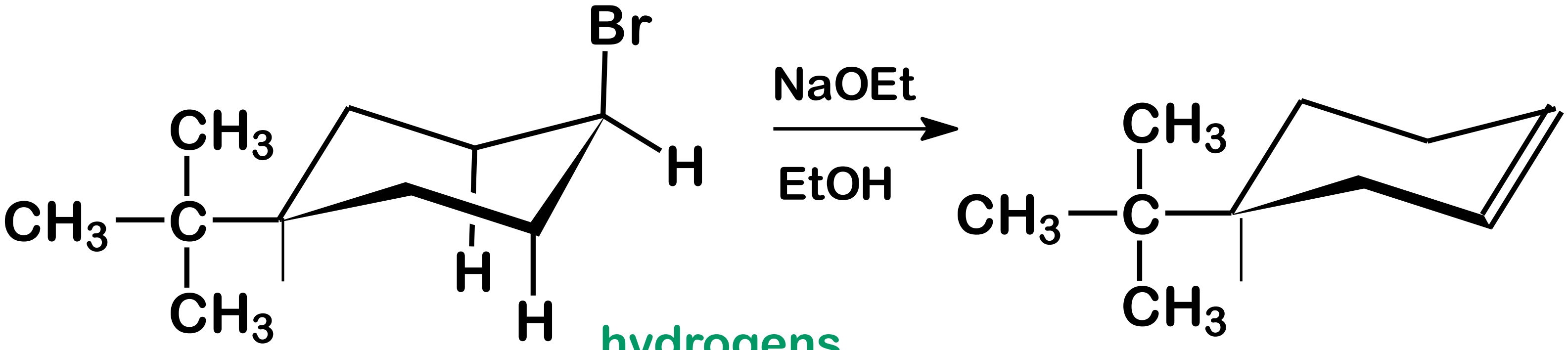
REACTION DOES NOT OCCUR EASILY IF ANTI-COPLANAR GEOMETRY CANNOT BE ACHIEVED

trans e,e



Br is not axial,
no anti-coplanar H

no reaction



hydrogens
equivalent

cis e,a

THESE RINGS WILL NOT INVERT

(WHYNOT ?)

E2

ALKYL HALIDES + STRONG BASE + HEAT

……. continued

SUMMARY TO DATE

ELIMINATION REACTIONS OF ALKYL HALIDES

STRONG BASE Required

HEAT Usually required

REGIOSELECTIVE

Follows Zaitsev Rule (Unless Stereochemistry Prevents)

- favors most substituted alkene

STEREOSPECIFIC

β-H and X must be ANTI-COPLANAR

- acyclics may have to rotate
- rings may have to invert

RATE EXPRESSIONS

exponents

$$\text{RATE} = K\,[A]^{n}\,[B]^{m}$$

rate “constant”

concentrations of reactants
A and B in moles / liter

Actually will change with temperature and solvent, the specific molecule, etc.

REACTION ORDER = SUM OF EXPONENTS = n + m

Not all reactants will necessarily show up in the rate expression.

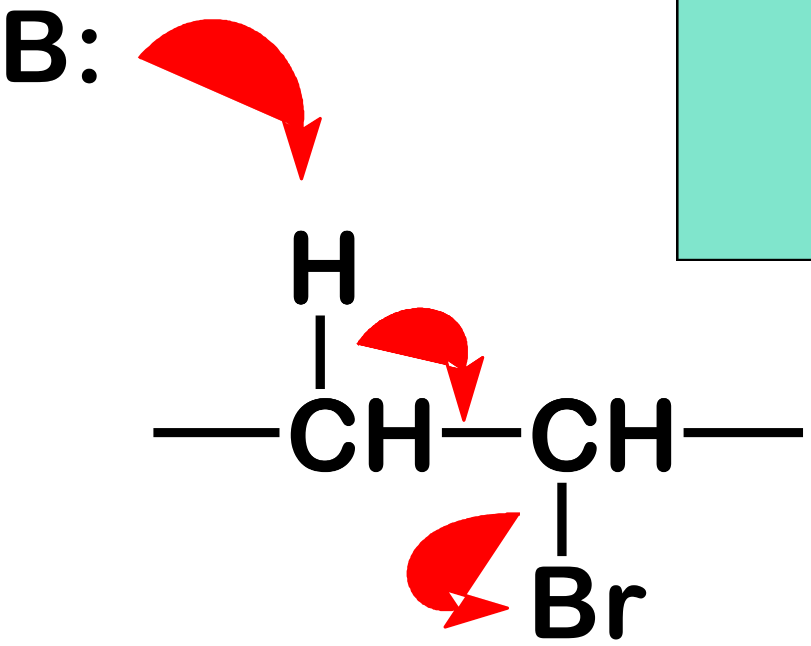
Fractional rate orders are possible : $\text{RATE} = K\,[A]^{3/2}\,[B]^{2}$

ميكانيكية التفاعل

انتزاع
ثنائي الجزيء

E2

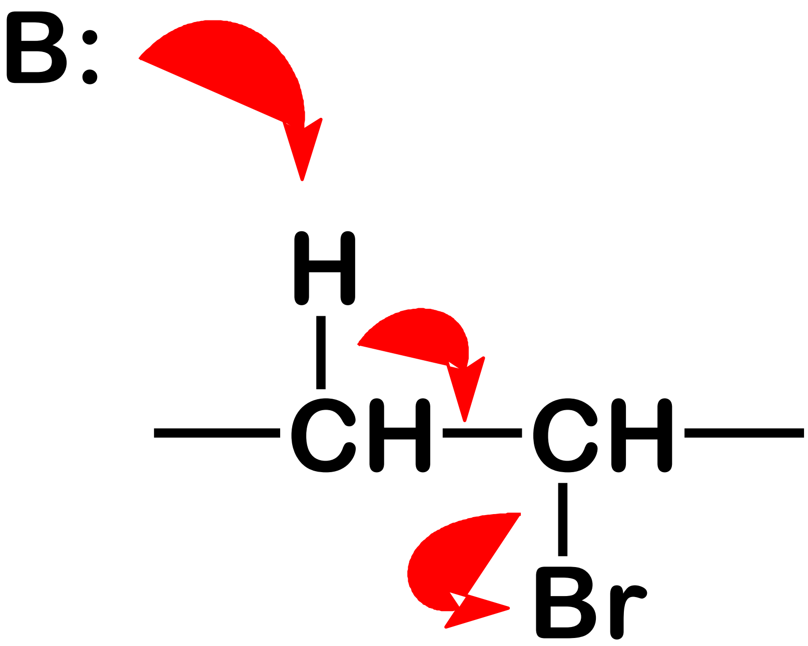
strong
base



alkyl
halide

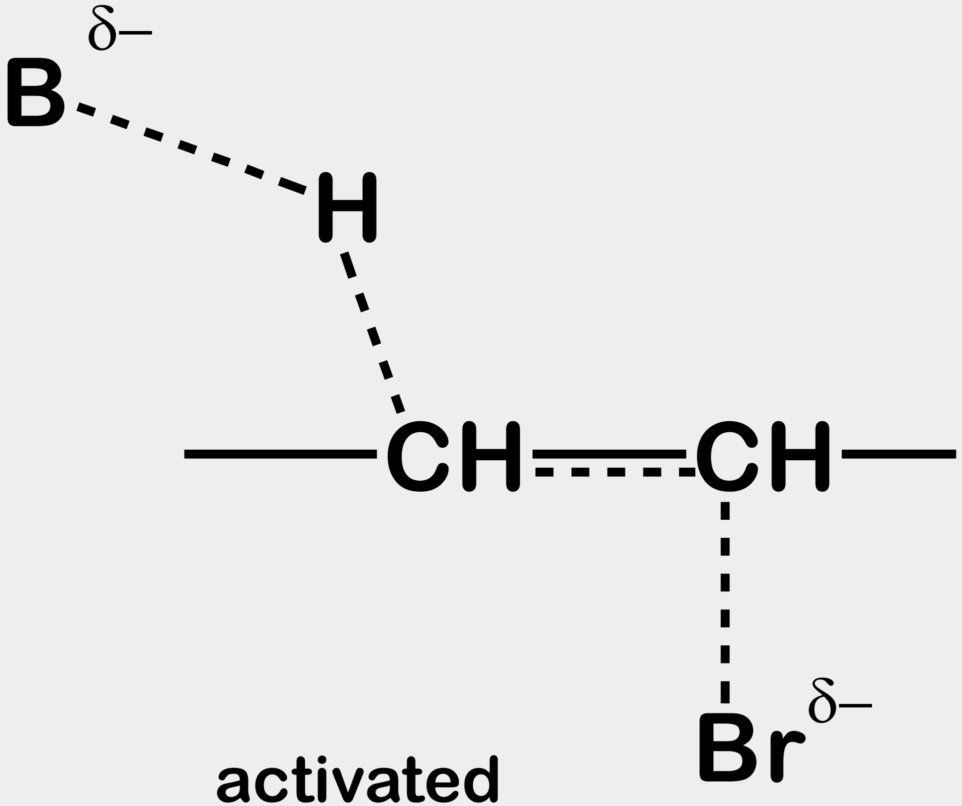
CONCERTED = only one step
All bonds are broken and formed without the formation of any intermediates.

E2 ELIMINATION

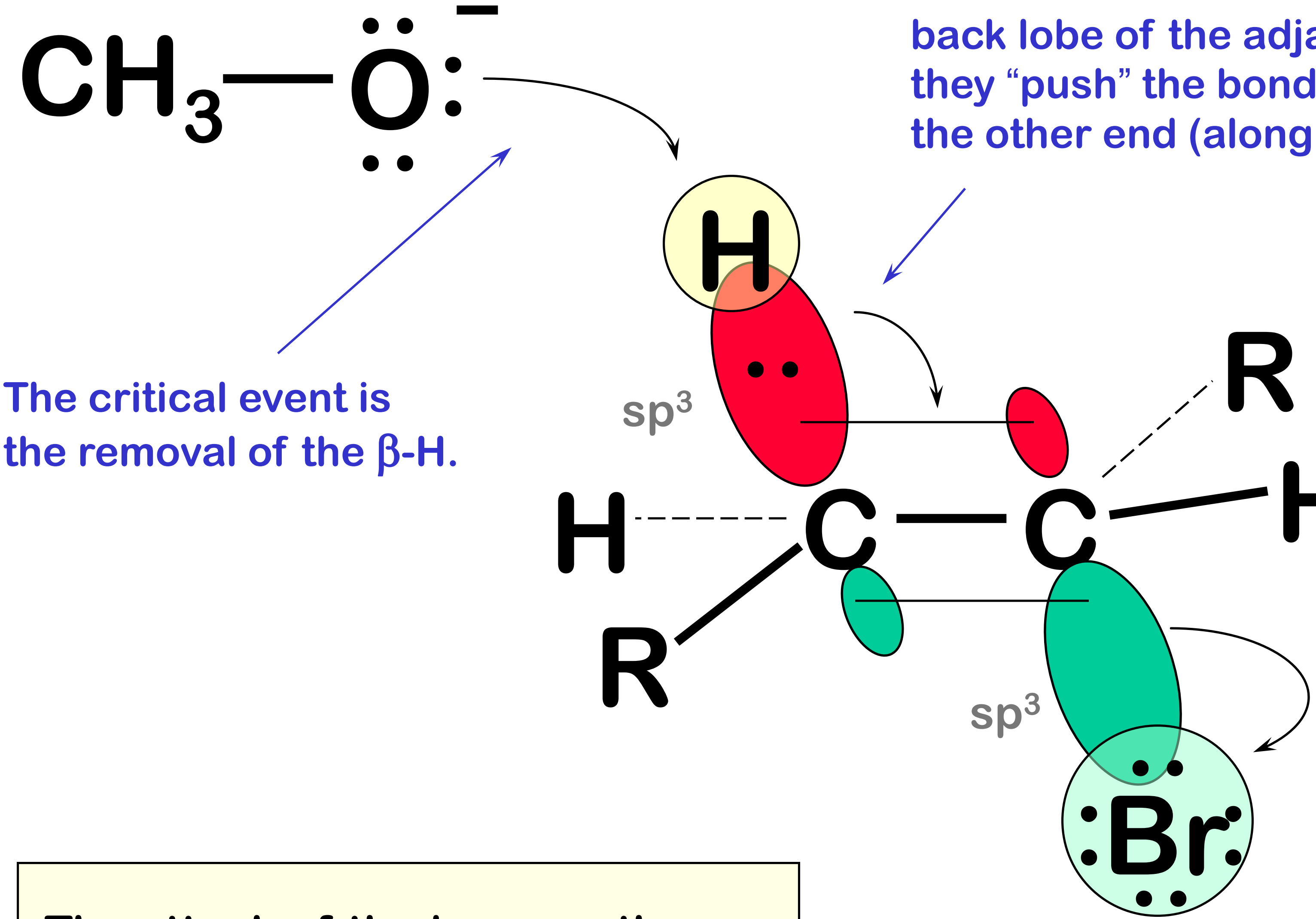


mechanism

Concerted : everything happens at once without any intermediates.



activated complex



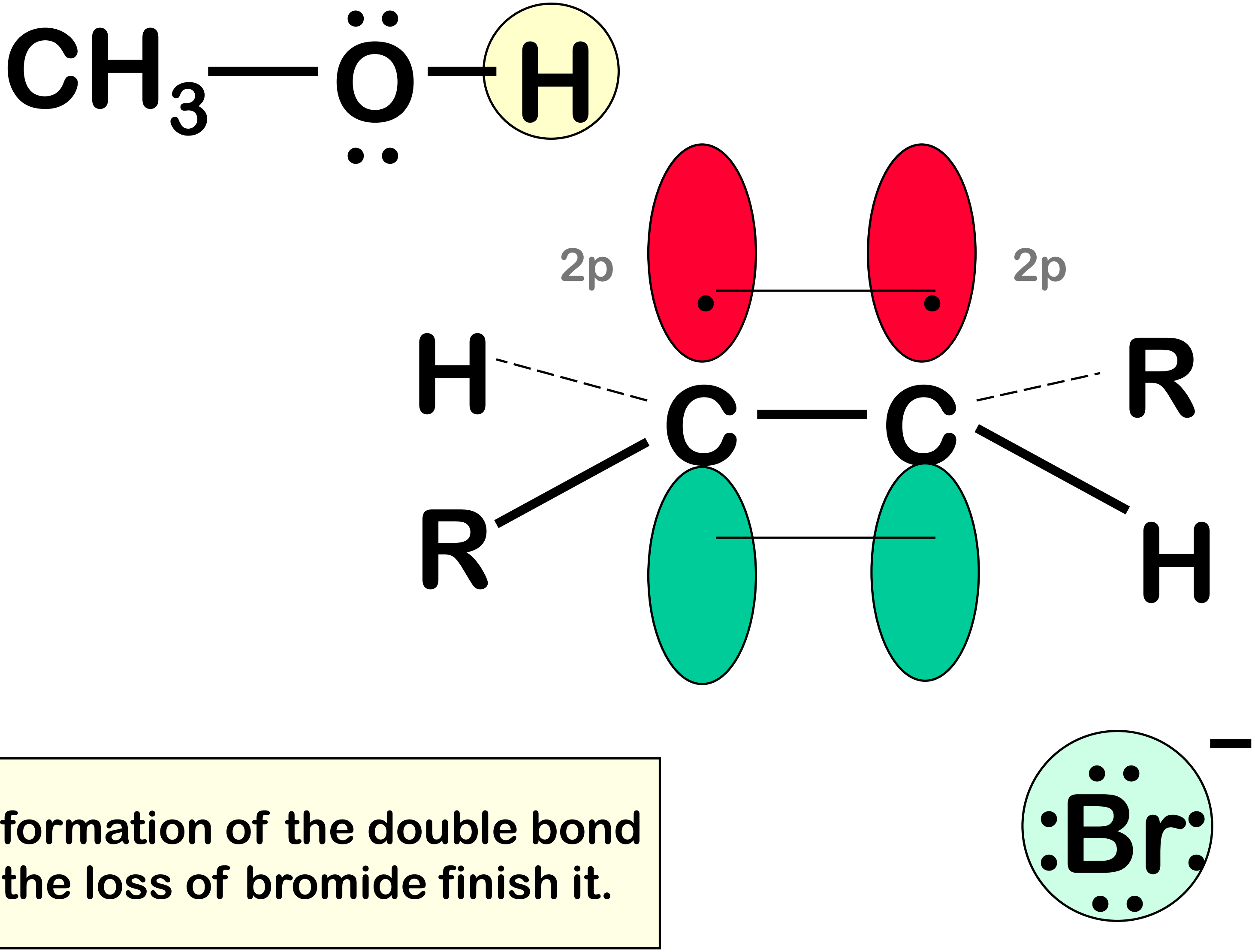
When these electrons enter the back lobe of the adjacent orbital they “push” the bonding pair out the other end (along with Br).

The critical event is the removal of the β-H.

Notice the parallel aligment of the two sp^3 orbitals.

The attack of the base on the β-hydrogen starts the reaction.

Note the parallel orbitals in the pi bond.



The formation of the double bond and the loss of bromide finish it.

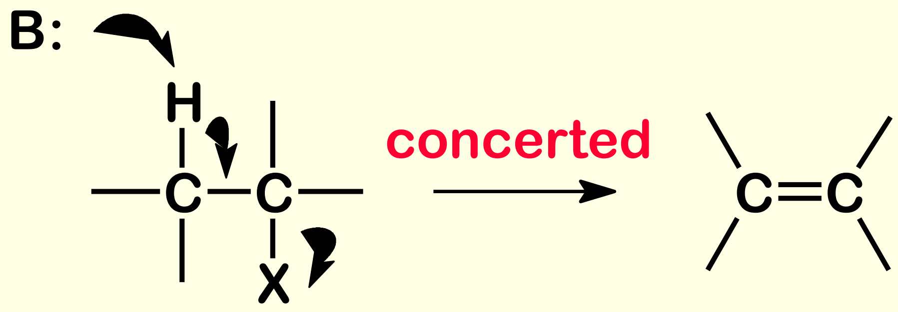
النوع الثاني من الإنتزاع E1
OTHER ELIMINATION MECHANISMS

ELIMINATION

ANIMATED MECHANISM

ELIMINATION OF HALOGENOALKANES

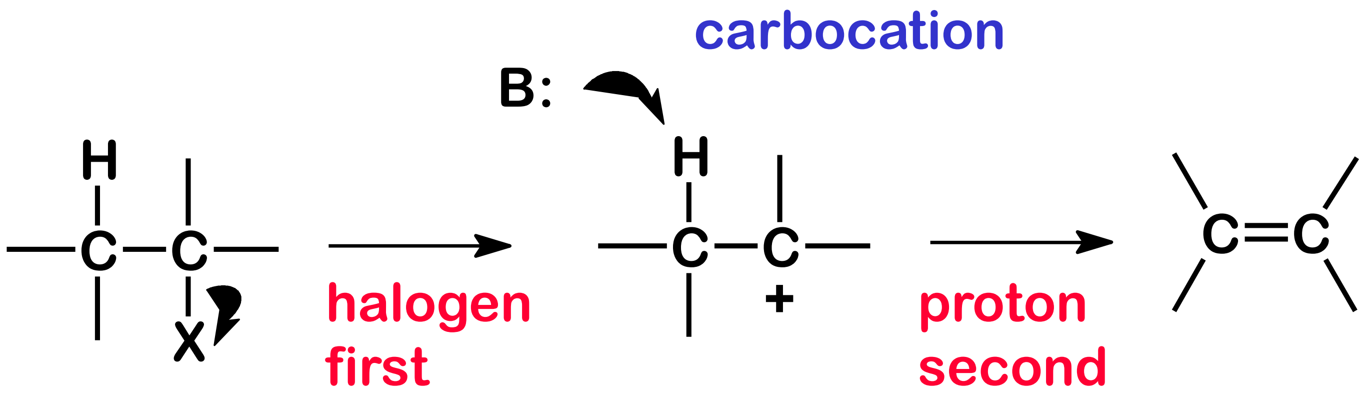
Three types of elimination reactions are conceivable



concerted

just studied

E2

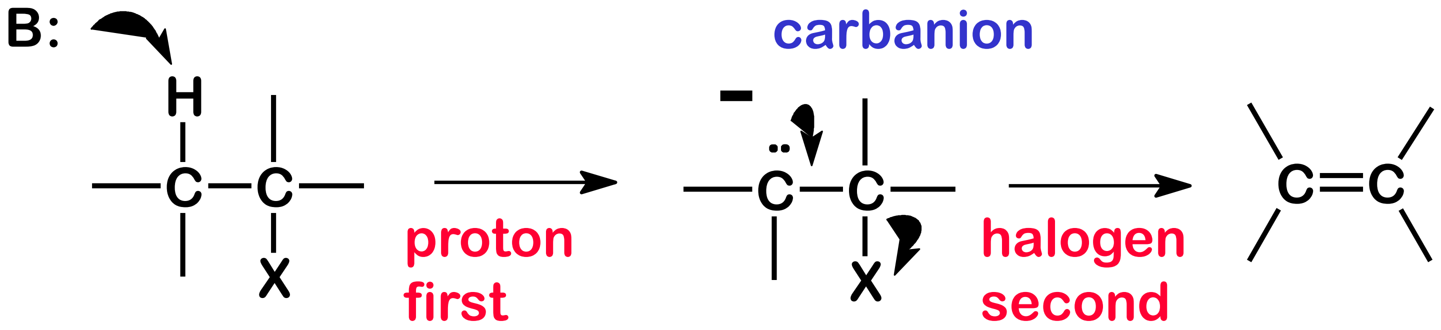


carbocation

halogen first

proton second

E1



carbanion

proton first

halogen second

E1cb

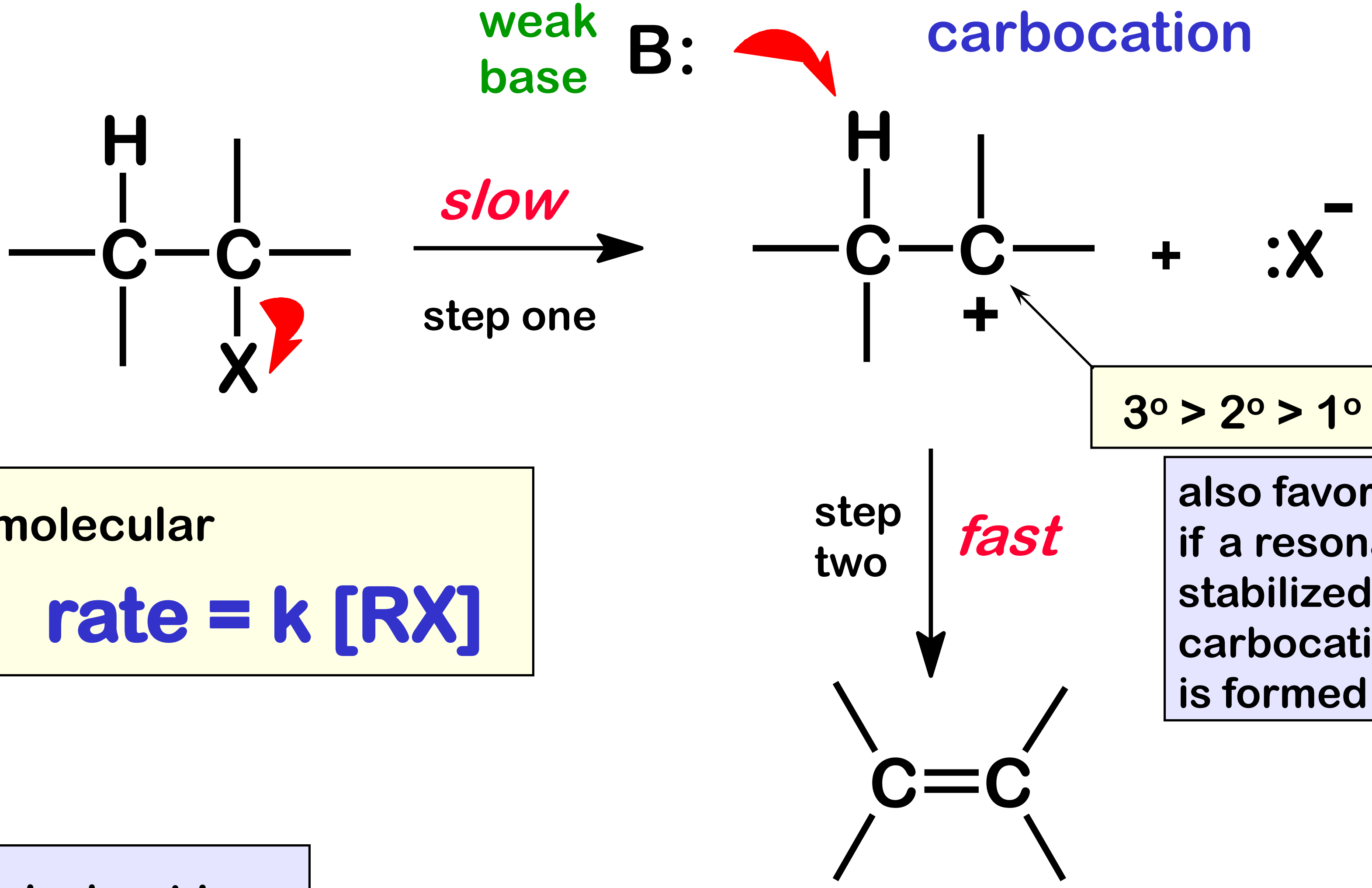
E1

ALKYL HALIDES + WEAK BASE
(SOLVOLYSIS)

The removal of a β-hydrogen becomes difficult without a strong base and a different mechanism (ionization) begins to take place

….. if the substrate is capable.

The E1 Elimination Reaction (two steps)



$3^o > 2^o > 1^o$

also favored if a resonance stabilized carbocation is formed

unimolecular

rate = k [RX]

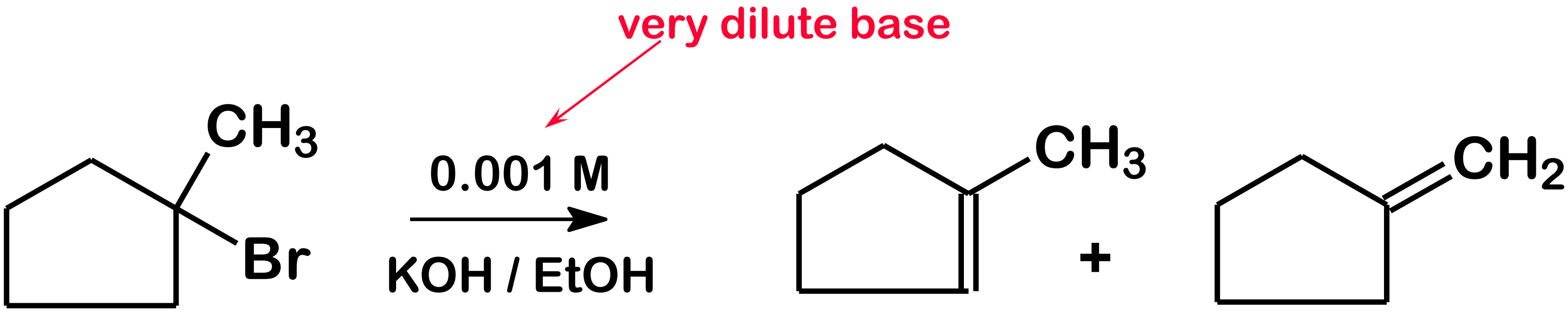
Works best in a polar solvent.

IONS FORMED

E1 REACTION IS REGIOSELECTIVE

THE ZAITSEV RULE IS FOLLOWED

(stereochemistry is not a problem as in E2)



major

minor

tertiary

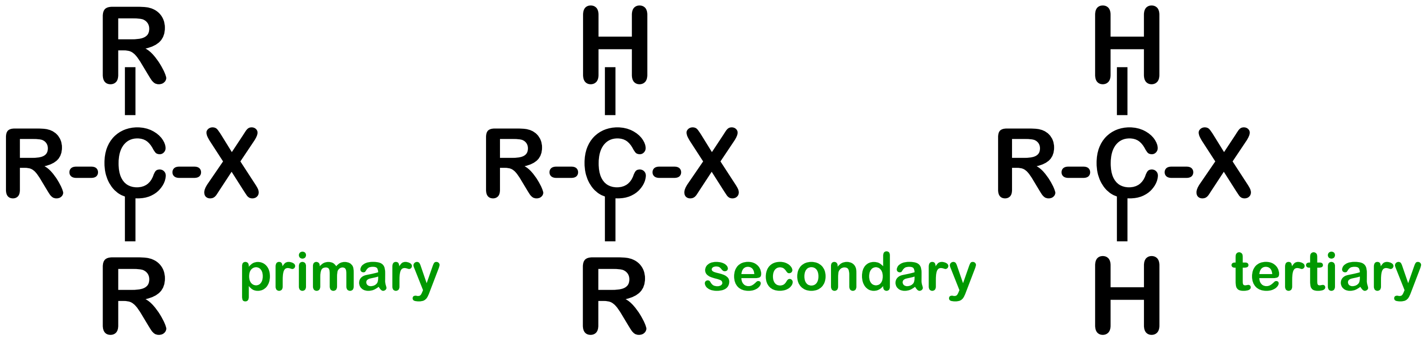
trisubstituted

Zaitsev

disubstituted

DIFFERENCES BETWEEN E1 AND E2

STRUCTURE OF SUBSTRATE

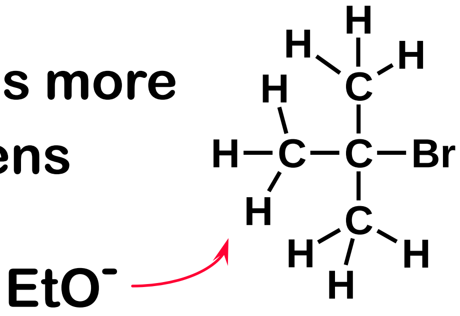


Obviously for E1 which forms a carbocation intermediate

rate : tertiary > secondary > primary > methyl

But this same order holds for E2 also.

tertiary has more
β -hydrogens



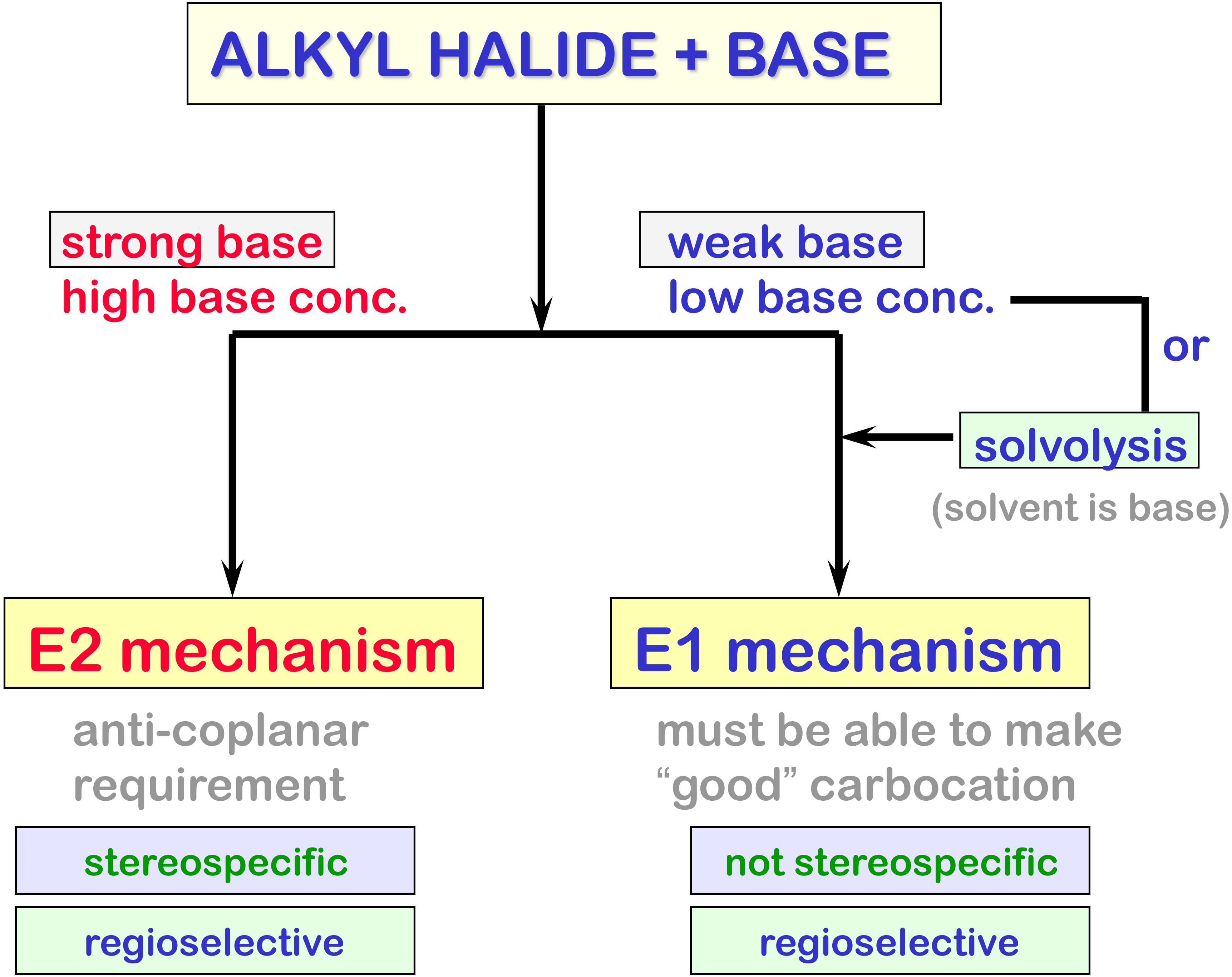
more opportunites
for reaction

WHEN THE E1 MECHANISM OCCURS

E1 occurs only

1) at zero or low base concentration
2) with solvolysis (the solvent is the base)
3) with tertiary and resonance capable substrates (alkyl halides)

If a strong base is present in moderate to high concentration, or the substrate is a primary halide, the E2 reaction dominates.



ALKYL HALIDE + BASE

strong base
high base conc.

weak base
low base conc.

or

solvolysis
(solvent is base)

E2 mechanism

anti-coplanar
requirement

stereospecific

regioselective

E1 mechanism

must be able to make
“good” carbocation

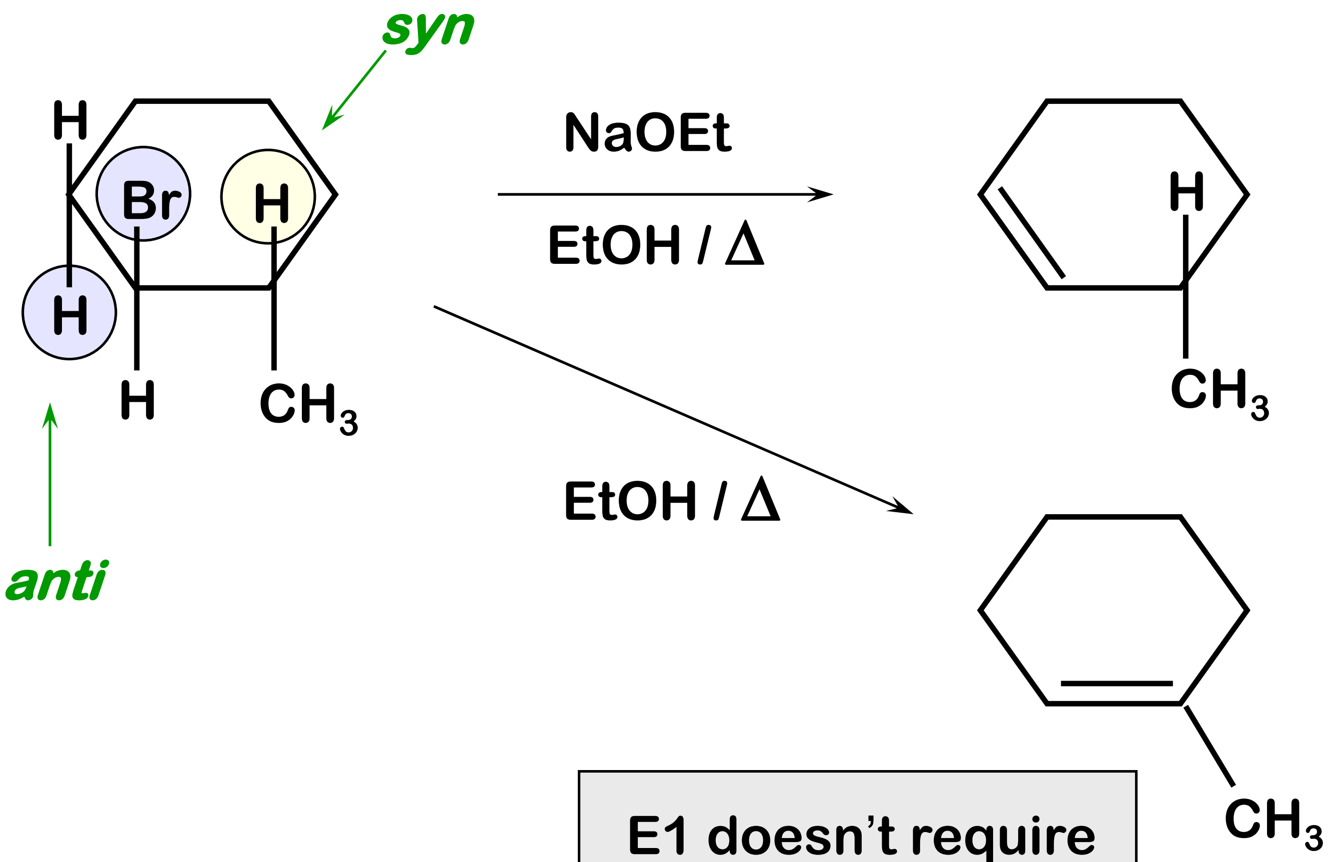
not stereospecific

regioselective

SOMETIMES E1 AND E2 RESULTS DIFFER

A COMPARISON OF E1 AND E2

major product



E2

Anti-Zaitsev

stereospecific
anti

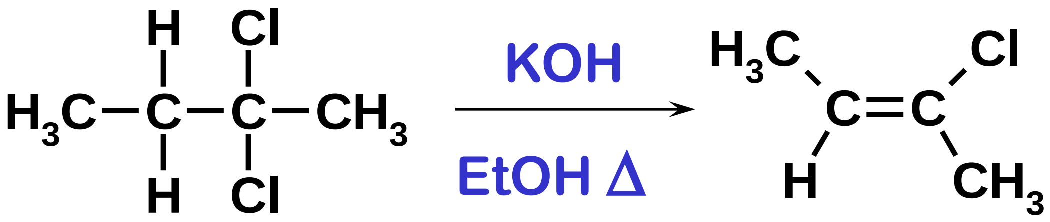
E1

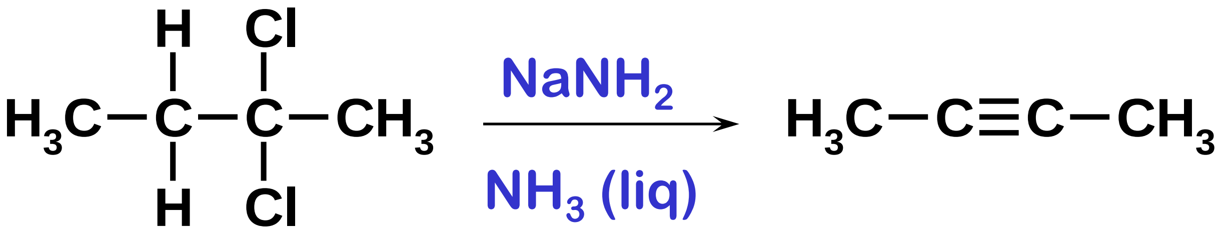
Zaitsev

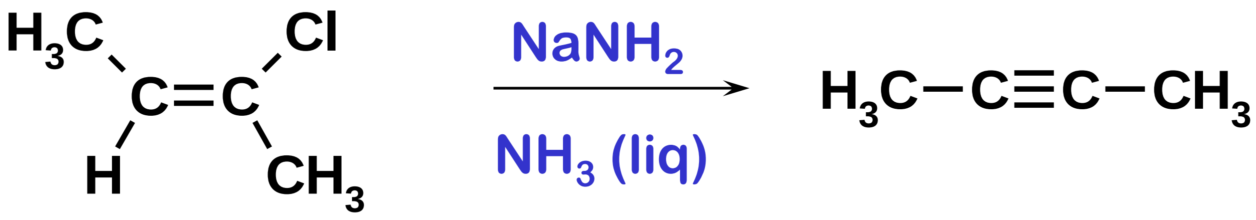
not
stereospecific

E1 doesn’t require
anti-coplanarity

EXAMPLES







trans

(the reaction is more difficult for *cis*)