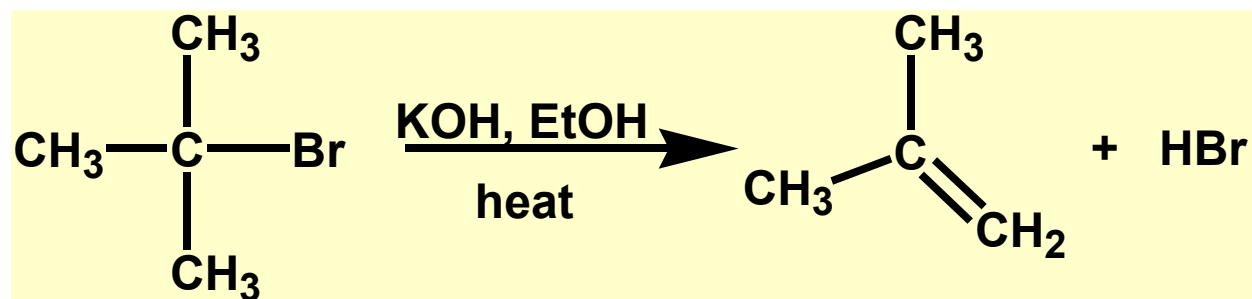


<http://196.3.3.103/courses/index.html>

ALKYL HALIDES – ELIMINATION REACTIONS

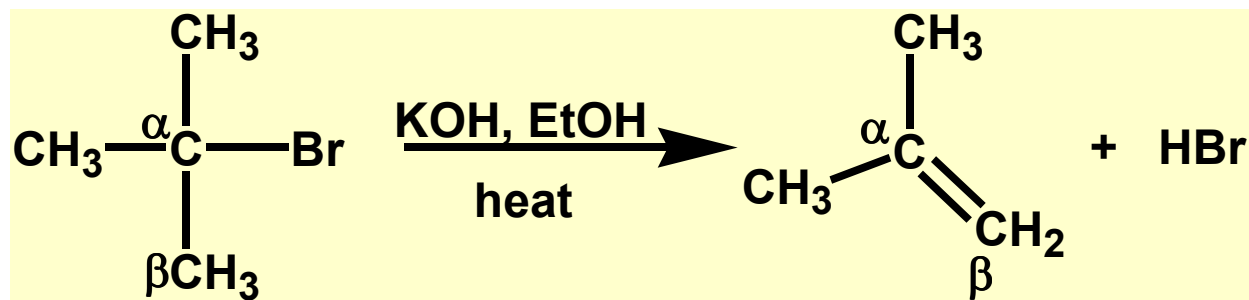
ALKYL HALIDES UNDERGO ELIMINATION OF HX WHEN TREATED WITH BASE. THE PRODUCTS ARE ALKENES.



ELIMINATION REACTIONS USUALLY REQUIRE FORCING CONDITIONS, I.E. HEAT AND STRONG BASE.

THE ELIMINATION REACTIONS WHICH ALKYL HALIDES UNDERGO ARE KNOWN AS **1,2-ELIMINATIONS OR β ELIMINATIONS**.

ALKYL HALIDES: ELIMINATION REACTIONS



The elements of H-X are lost from neighboring carbon atoms and a C=C is formed. The head carbon of the alkyl halide is termed α (“alpha”) and the carbon atom or atoms next to it are designated β (“beta”).

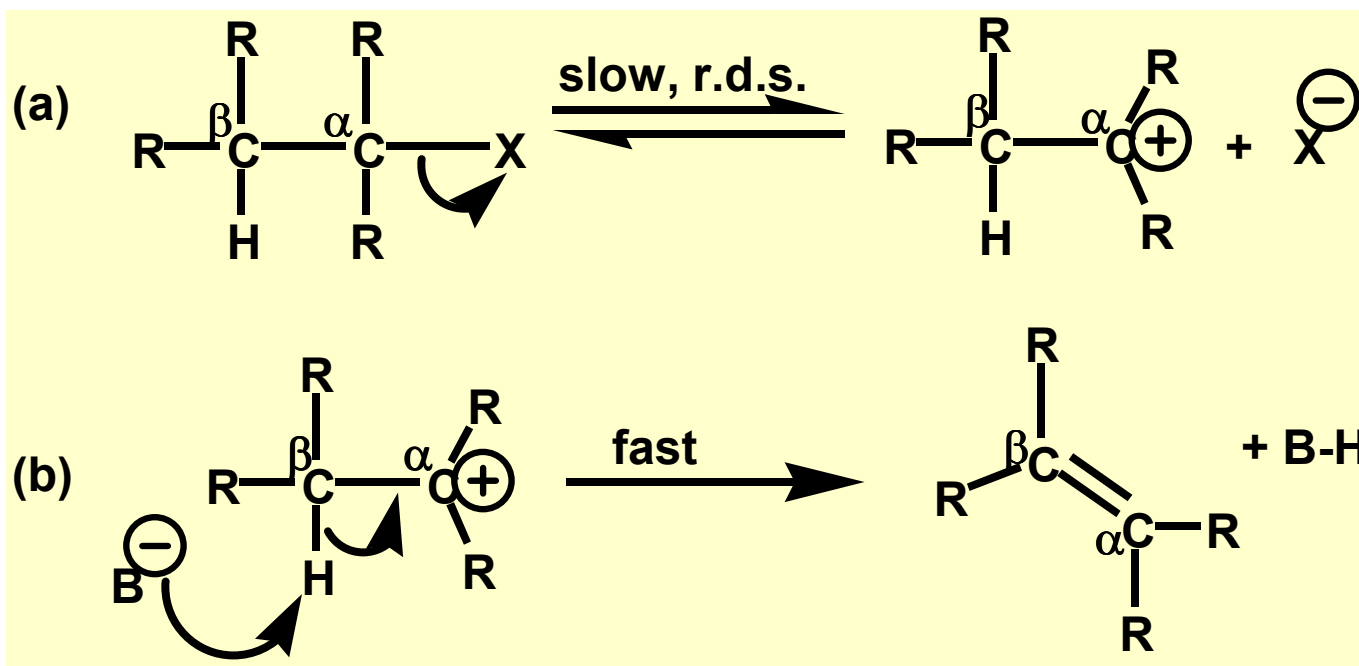
The halogen atom is lost from the α carbon, and the hydrogen from one of the β carbons.

ALKYL HALIDES: ELIMINATION REACTIONS

THE TWO MOST IMPORTANT MECHANISMS
BY WHICH ALKYL HALIDES UNDERGO
ELIMINATION REACTIONS ARE:

1. **THE E1 MECHANISM (UNIMOLECULAR);**
2. **THE E2 MECHANISM (BIMOLECULAR).**

ELIMINATION REACTIONS OF ALKYL HALIDES: THE UNIMOLECULAR MECHANISM (E1)



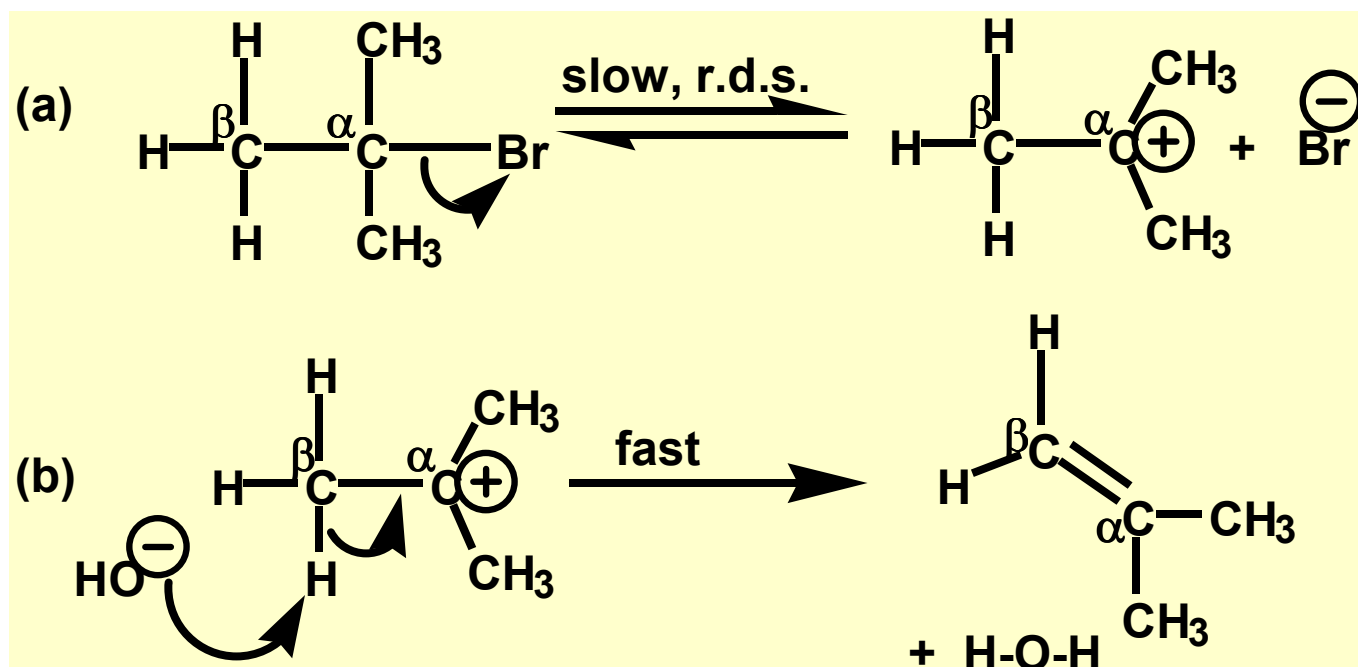
The slow, rate determining step entails one species – the alkyl halide.

The rate of the reaction = $k[\text{alkyl halide}]$

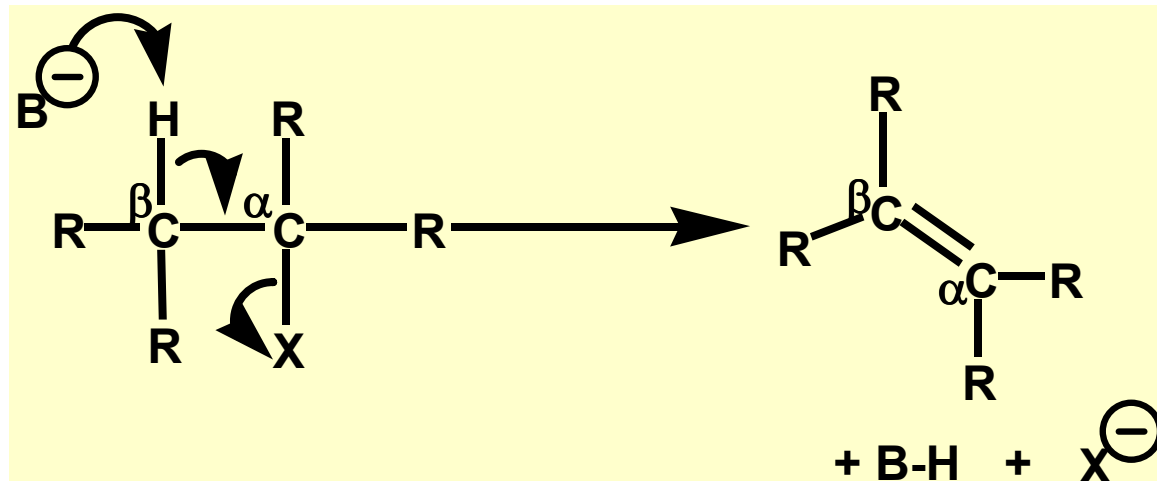
Note the carbocation intermediate

ELIMINATION REACTIONS OF ALKYL HALIDES: THE UNIMOLECULAR MECHANISM (E1)

A *carbocation intermediate* is formed when alkyl halides undergo elimination via the E1 (unimolecular) mechanism. 3° alkyl halides are likely to lose HX via this mechanism. For *t*-butyl bromide in aqueous alcoholic KOH:



ELIMINATION REACTIONS OF ALKYL HALIDES: THE BIMOLECULAR MECHANISM (E2)



THIS IS A **CONCERTED** REACTION.

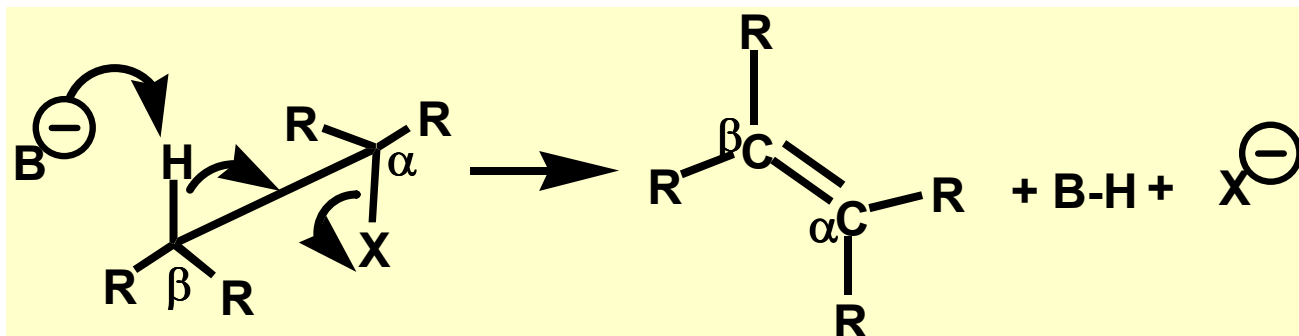
BOND FORMATION AND BOND BREAKING TAKE
PLACE SIMULTANEOUSLY.

THE RATE DETERMINING STEP ENTAILS THE BASE AND
THE ALKYL HALIDE.

$$\text{RATE} = k[\text{alkyl halide}][\text{base}]$$

THE BIMOLECULAR MECHANISM (E2) A VERY IMPORTANT FEATURE

For an alkyl halide to undergo elimination via the E2 mechanism, the H and X groups must be *anti* to each other and be in the same plane with each other and the carbon atoms to which they are attached.



THE ELEMENTS OF H-X MUST BE
ANTIPERIPLANAR.

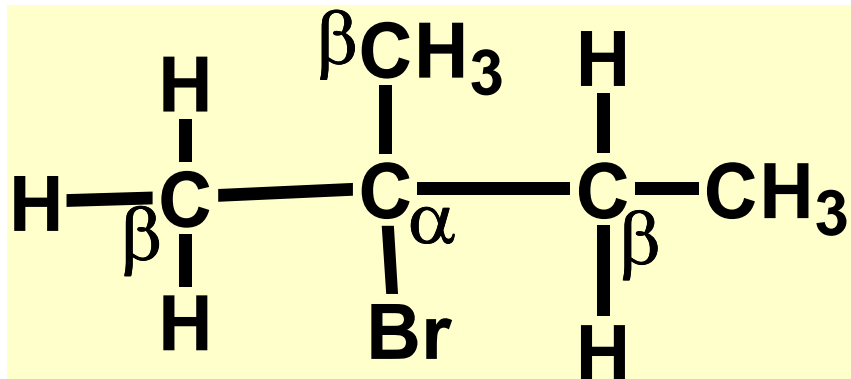
OTHER ASPECTS OF E1 AND E2 REACTIONS

1. THE DISTINCTION BETWEEN THE E1 AND E2 MECHANISMS IS NOT AS CLEAR AS THE DISTINCTION BETWEEN THE S_N1 AND S_N2 MECHANISMS.
2. 3° AND 2° ALKYL HALIDES WILL ELIMINATE H-X VIA BOTH THE E1 AND E2 MECHANISMS.
THE ELIMINATION OF H-X FROM 1° ALKYL HALIDES TAKES PLACE VIA THE E2 MECHANISM ONLY.
FOR BOTH E1 AND E2 MECHANISMS, THE RATES FOLLOW THE TREND:
3° R-X > 2° R-X > 1° R-X (do not react via E1)

OTHER ASPECTS OF E1 AND E2 REACTIONS

3. FOR MANY ALKYL HALIDES, THERE ARE TWO POSSIBLE ELIMINATION PRODUCTS.

THE 3° ALKYL HALIDE BELOW HAS THREE β CARBONS; TWO ARE IDENTICAL METHYL (CH_3) GROUPS, AND THE THIRD IS A METHYLENE (CH_2) GROUP.

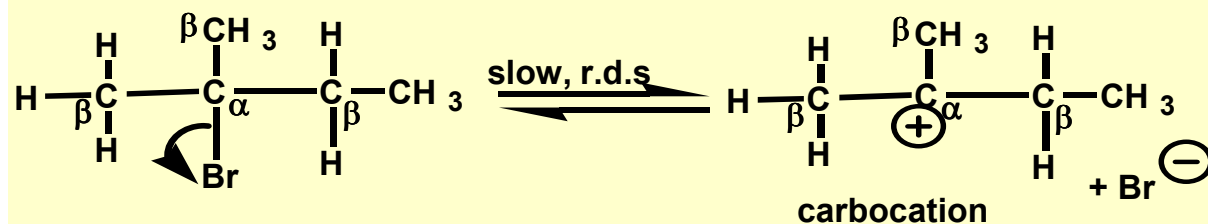


LET US EXAMINE THE ELIMINATION OF H-Br FROM THIS COMPOUND VIA THE E1 MECHANISM.

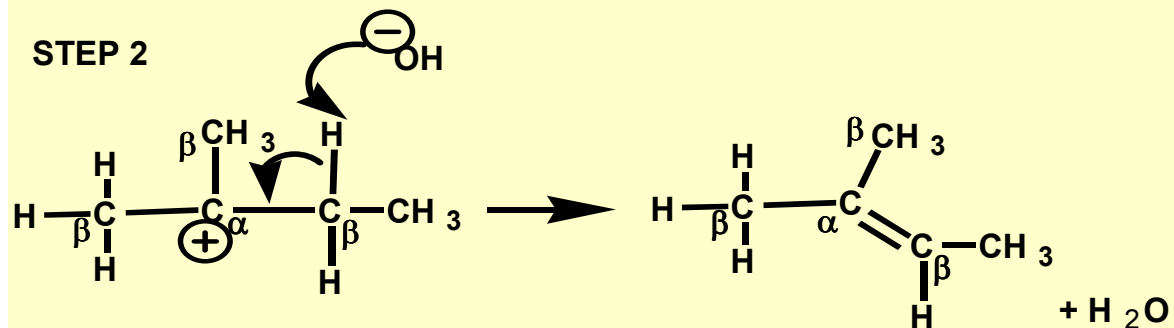
ELIMINATION PRODUCTS: E1 MECHANISM

Two products can result from the loss of H-Br

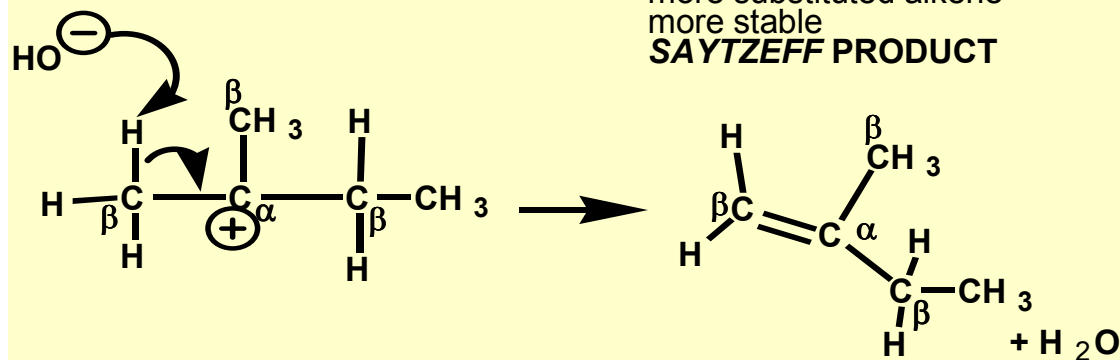
STEP 1



STEP 2



and/or



more substituted alkene
more stable
SAYTZEFF PRODUCT

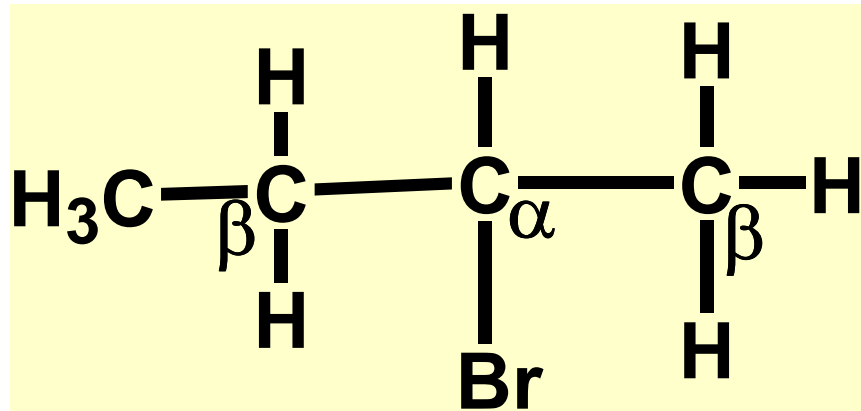
less substituted alkene
less stable
HOFMANN PRODUCT

ELIMINATION PRODUCTS: E2 MECHANISM

THE 2° ALKYL HALIDE SHOWN BELOW HAS TWO β CARBONS WHICH ARE NOT IDENTICAL.

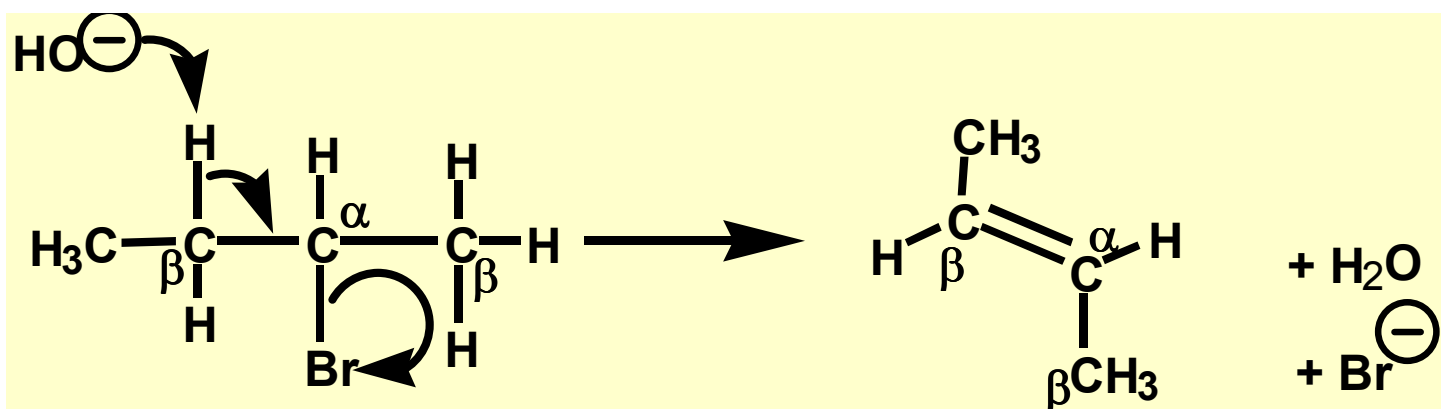
ONE IS A METHYL (CH_3) GROUP AND THE OTHER IS A METHYLENE (CH_2) GROUP.

LET US EXAMINE THE ELIMINATION OF H-Br FROM THIS COMPOUND VIA THE E2 MECHANISM.



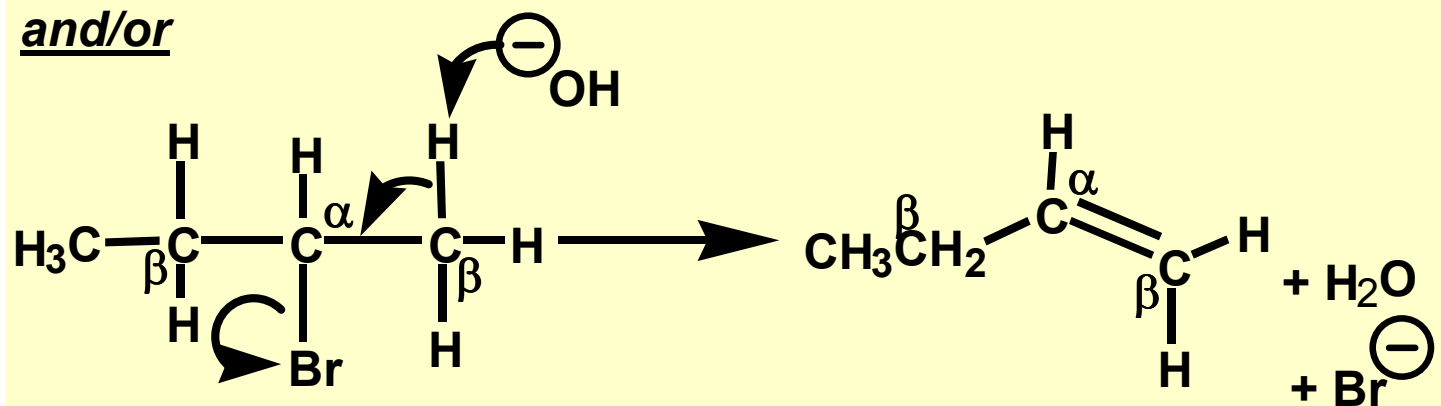
ELIMINATION PRODUCTS: E2 MECHANISM

TWO PRODUCTS CAN FORM VIA THE E2 MECHANISM



more substituted alkene
more stable
SAYTZEFF PRODUCT

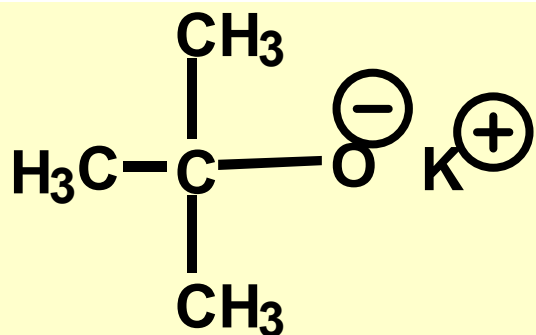
and/or



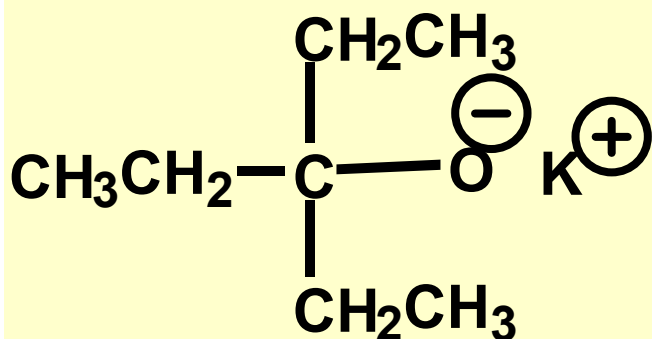
less substituted alkene
less stable
HOFMANN PRODUCT

ELIMINATION PRODUCTS: HOFMANN VS. SAYTZEFF

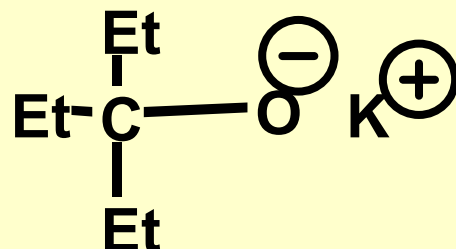
THE PROPORTION OF THE LESS SUBSTITUTED ALKENE (HOFMANN PRODUCT) CAN BE INCREASED BY USING A VERY BULKY BASE. TWO EXAMPLES OF BULKY BASES ARE SHOWN



potassium *t*-butoxide

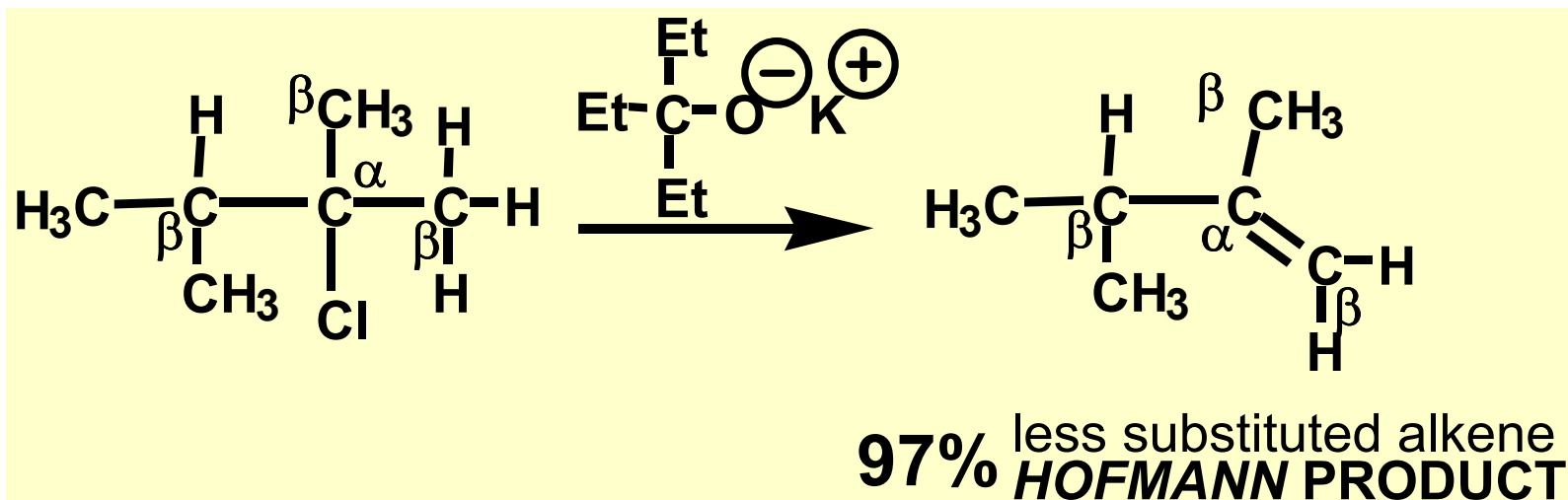


potassium 3-ethyl-3-pentoxide



ELIMINATION PRODUCTS: HOFMANN VS. SAYTZEFF

BULKY BASES INCREASE THE PROPORTION OF THE LESS SUBSTITUTED ALKENE (HOFMANN PRODUCT) FORMED IN ELIMINATION REACTIONS.

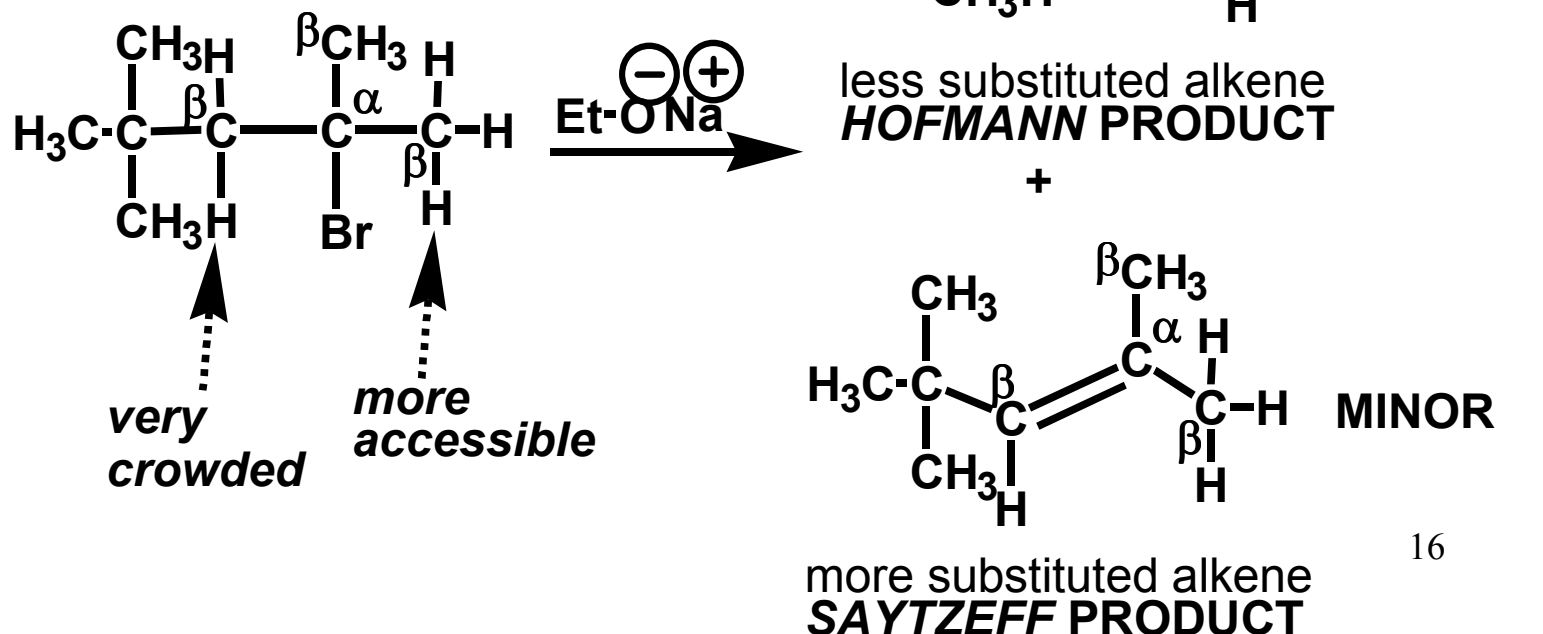


The H's on the less substituted β carbon are more sterically accessible to the base than are the H's on the more substituted β carbon. When the base is very bulky, then the H's on the less substituted β carbon are almost exclusively removed, and the less substituted (Hofmann) alkene product predominates.

ELIMINATION PRODUCTS: HOFMANN VS. SAYTZEFF

STERIC ACCESSIBILITY OF THE β H AFFECTS THE OUTCOME OF ELIMINATION REACTIONS.

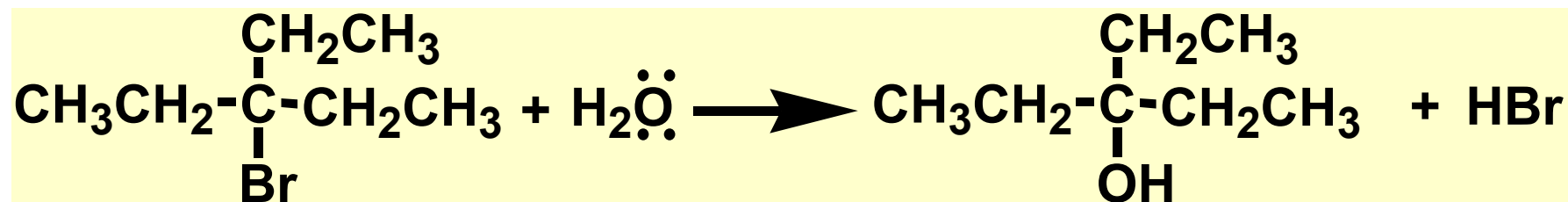
If the H on the β carbon whose elimination leads to the more substituted alkene is very crowded, then the proportion of the less substituted alkene product will be high.



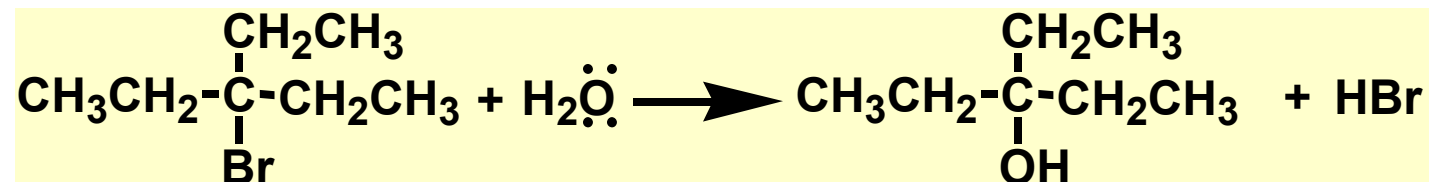
SUBSTITUTION VERSUS ELIMINATION: S_N1 VS E1

When substitution reactions are carried out on 3° alkyl halides (S_N1 reactions), products of elimination (alkenes) are almost inevitably formed.

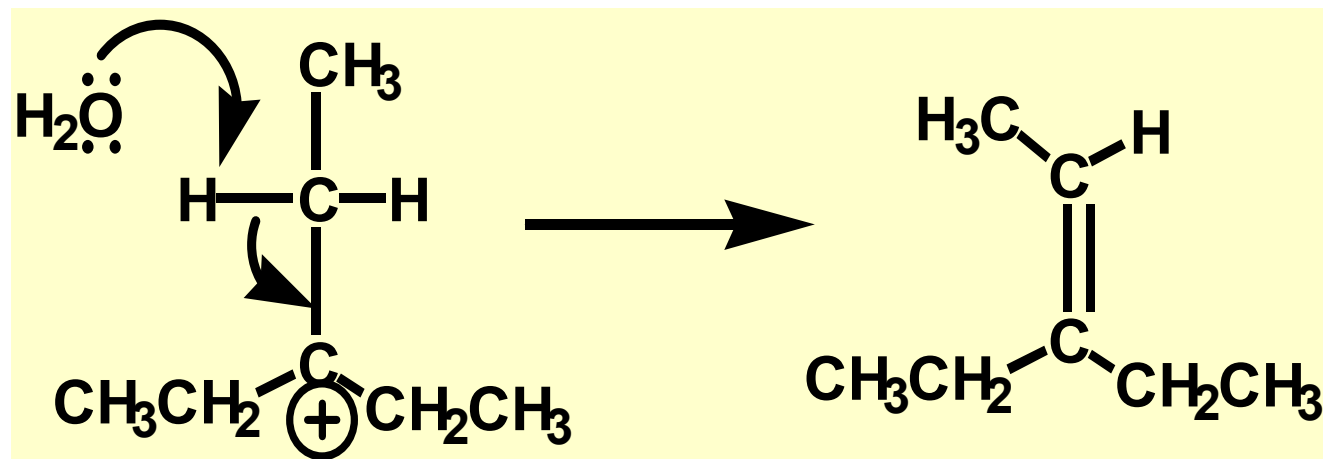
Let us consider the the following reaction.



SUBSTITUTION VERSUS ELIMINATION: S_N1 VS E1



In this reaction the carbocation intermediate, once it is formed, can lose a proton by reaction with as weak a base as H₂O to give appreciable quantities of the alkene (elimination) product.



SUBSTITUTION VERSUS ELIMINATION: E2 VS S_N2

IT IS EASIER TO CREATE CONDITIONS WHICH FAVOR THE E2 MECHANISM OVER THE S_N2 MECHANISM, OR *VICE VERSA*.

VERY STRONG BASE

(ETHOXIDE AS OPPOSED TO HYDROXIDE)

RELATIVELY NON-POLAR SOLVENTS

(E.G. ETHANOL IN PREFERENCE TO WATER)

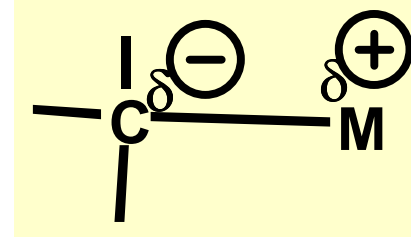
HIGHER TEMPERATURES, WILL FAVOR THE E2 MECHANISM OVER THE S_N2 MECHANISM.

ORGANOMETALLIC COMPOUNDS

COMPOUNDS IN WHICH A METAL IS DIRECTLY BONDED TO CARBON ARE KNOWN AS

ORGANOMETALLIC COMPOUNDS.

THE METAL-CARBON BOND IS POLARIZED AS SHOWN.



METALS ARE LESS ELECTRONEGATIVE THAN CARBON; LARGER DIFFERENCES IN ELECTRONEGATIVITY BETWEEN THE METAL AND CARBON INCREASE THE IONIC CHARACTER OF THE METAL-CARBON BOND. IONIC CHARACTER OF METAL CARBON BONDS FOLLOWS THE TREND



ORGANOMETALLIC COMPOUNDS

ALKYL DERIVATIVES OF ALMOST ALL METALS HAVE BEEN PREPARED.

THESE ARE NAMED AS “ALKYLMETALS”

$(\text{CH}_3)_2\text{Hg}$ **DIMETHYLMERCURY**

(liquid; bp 92 °C; neurotoxin; environmental contaminant)

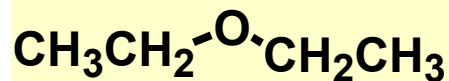
$(\text{CH}_3\text{CH}_2)_4\text{Pb}$ **TETRAETHYLLEAD**

(liquid; bp ~ 220 °C; toxic; formerly used as a gasoline additive)

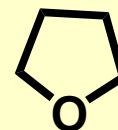
GRIGNARD REAGENTS

ALKYLMAGNESIUM HALIDES, R-Mg-X, ARE KNOWN AS **GRIGNARD REAGENTS**.

GRIGNARD REAGENTS ARE PREPARED BY REACTING ALKYL HALIDES WITH EXCESS MAGNESIUM METAL IN DRY ALCOHOL-FREE DIETHYL ETHER OR TETRAHYDROFURAN (THF). DIETHYL ETHER AND THF ARE SOLVENTS.



diethyl ether



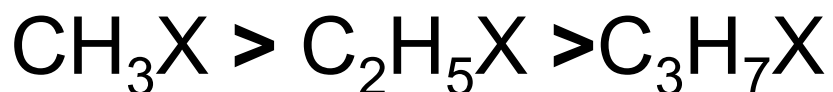
tetrahydrofuran
(THF), a cyclic ether

GRIGNARD REAGENTS

PREPARATION



Ease of formation follows the trends shown below



Grignard reagents are usually closely associated with two molecules of the ethereal solvent in which they have been prepared.

