

Alkenes

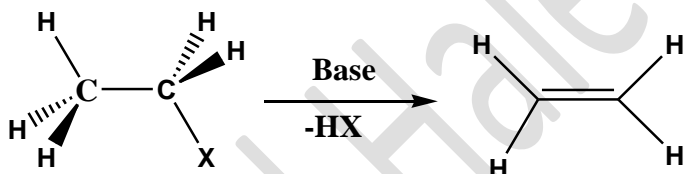
Hydrocarbons whose molecules contain the carbon-carbon double bond are called alkenes. An old name for this family of compounds that is still often used is the name olefins. Ethene (ethylene), the simplest olefin, was called olefiant gas (Latin: *Oleum*, oil and *facere*, to make) because gaseous ethene reacts with chlorine to form dichloroethane, a liquid oil.

Synthesis of alkenes

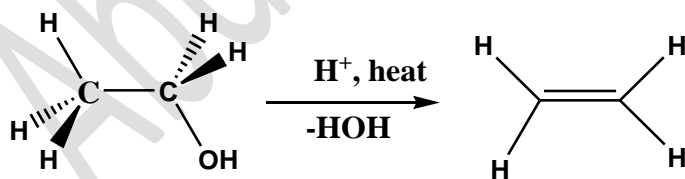
Elimination reactions

Since an elimination reaction can introduce a double bond into a molecule, elimination reactions can be widely used for synthesizing alkenes. Various elimination reactions used for synthesizing alkenes include:

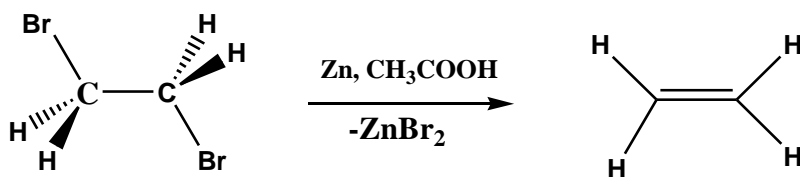
1. Dehydrohalogenation of alkyl halides



2. Dehydration of alcohols

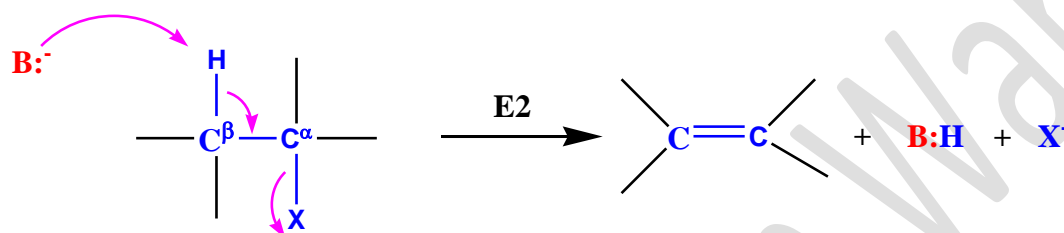


3. Debromination of vicinal dibromides



Dehydrohalogenation of Alkyl Halides

Synthesis of an alkene by dehydrohalogenation is almost always better achieved by an E2 reaction.



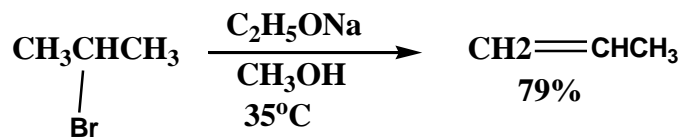
The E1 mechanism is too variable and too many competing events are possible. One of the competing reactions is the rearrangement of the carbon skeleton. For an E2 reaction secondary or tertiary alkyl halide must be used. To avoid E1 condition a high concentration of a strong, relatively non polarizable base such as an alkoxide ion is used and a relatively non polar solvent such as an alcohol. Relatively high temperature is used to favour elimination generally. The typical reagents for dehydrohalogenation are sodium ethoxide in ethanol and potassium tert-butoxide in tert-butyl alcohol. Potassium hydroxide in ethanol is also used some times; in this reaction the reactive bases probably include the ethoxide ion formed by the following equilibrium.

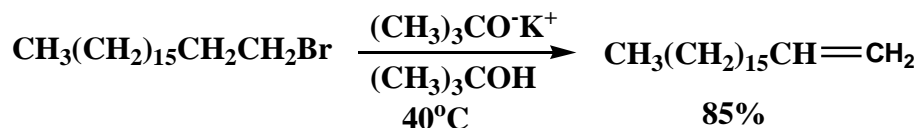
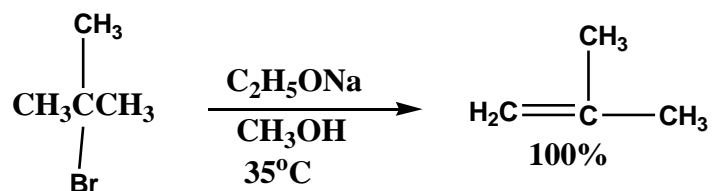


E2 Reactions: The Orientation of the Double Bond in the Product

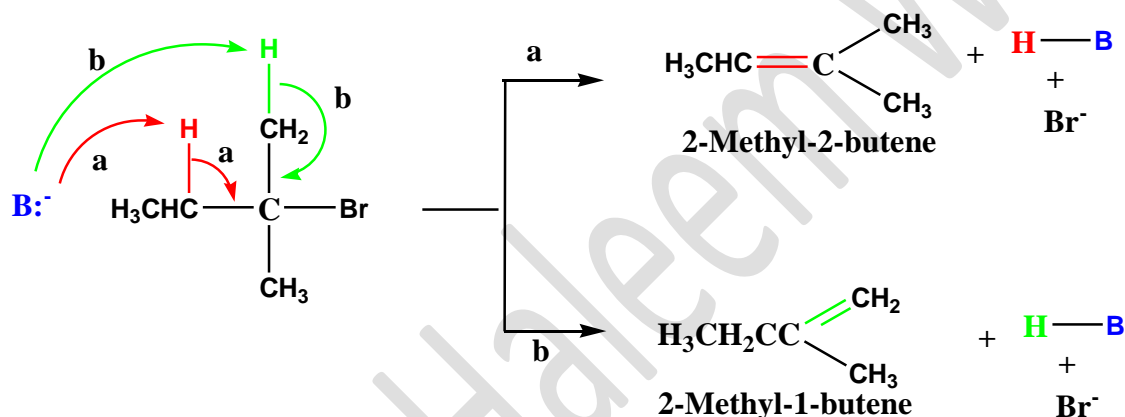
Zaitsev's Rule

In case of symmetric alkyl halides only a single elimination product is possible. For example:

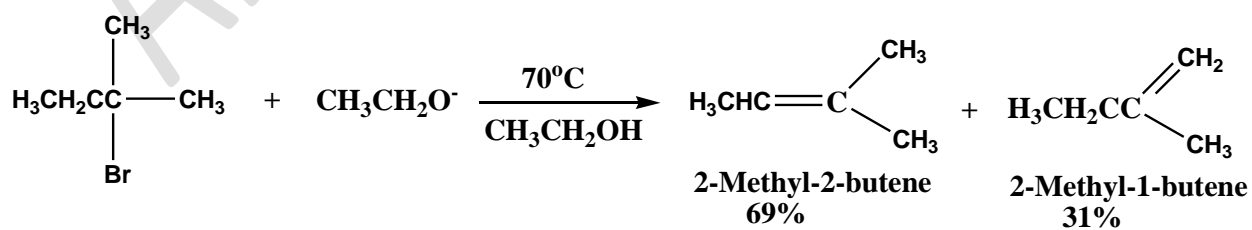




Dehydrohalogenation of many alkyl halides having more than one β hydrogens, however, can yield more than one product. For example, dehydrohalogenation of 2-bromo-2-methylbutane can yield two products: 2-methyl-2-butene and 2-methyl-1-butene.

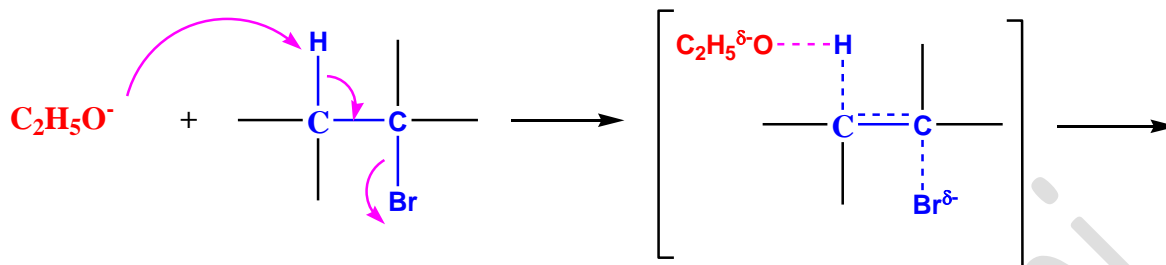


If a small base such as ethoxide ion or Hydroxide ion is used, the major product of the reaction will be the most stable alkene. The most stable alkene as we know has the more highly substituted double bond. Thus the major product is formed by abstraction of internal (2° or 3°) Hydrogen atom in preference to the external (1°) Hydrogen atom.

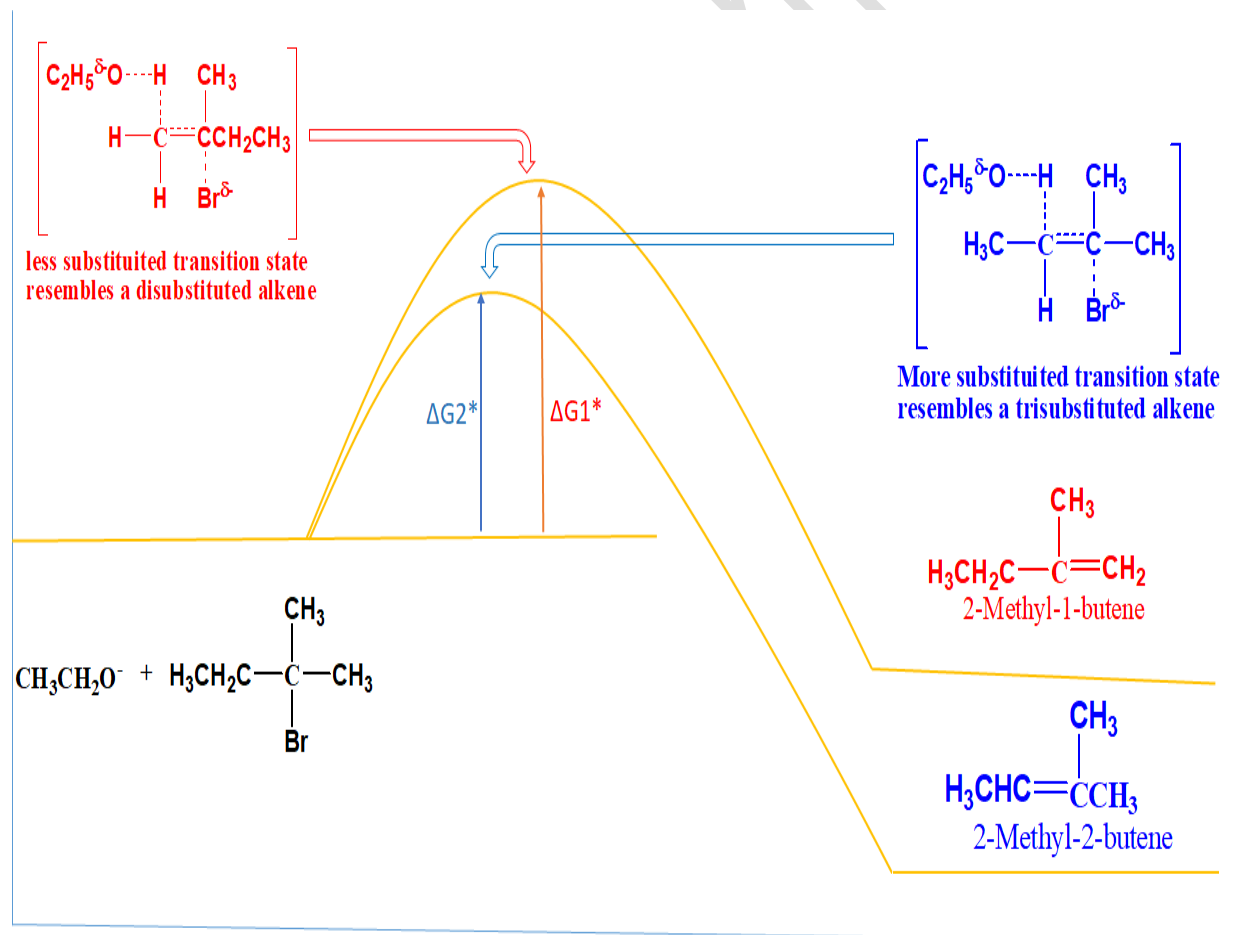
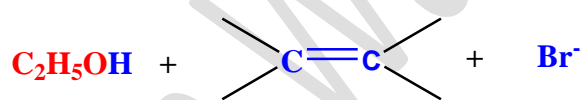


2-Methyl-2-butene is a trisubstituted alkene whereas 2-Methyl-1-butene is only disubstituted. Thus 2-Methyl-2-butene is the major product.

The reason for this behaviour appears to be related to the double bond character that develops in the transition state for each reaction.



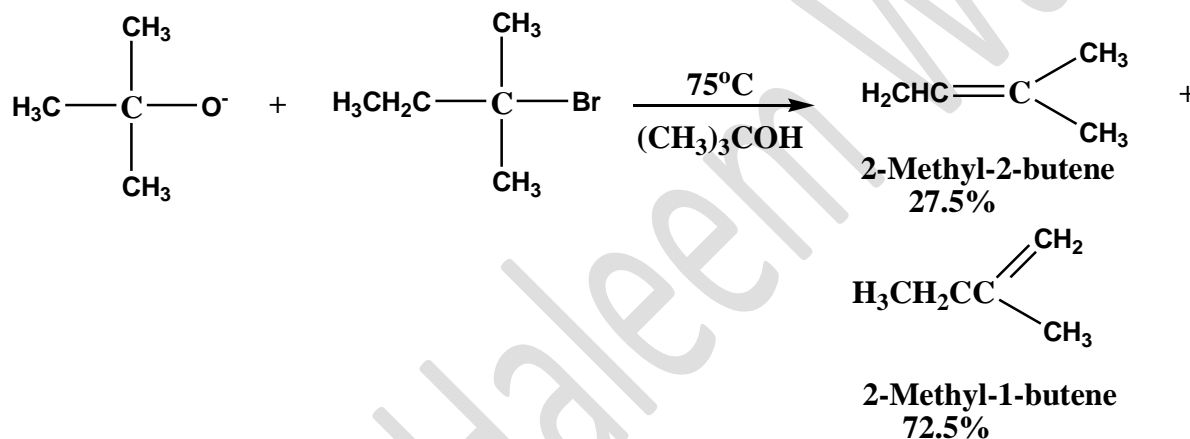
Transition state for an E2 reaction.
The carbon-carbon bond has some double bond character.



Since the transition state leading to 2-Methyl-2-butene methyl 2 butene resembles a more stable alkene, this transition state is more stable. The free energy of activation for this reaction is lower and 2-Methyl-2-butene is formed faster. These reactions are known to be under Kinetic control. Whenever an elimination reaction occurs to give the most stable, most highly substituted alkene, the elimination is said to follow the zaitsev's rule.

An Exception to Zaitsev's Rule- Hofmann Rule.

In case dehydrogenation is carried out with a bulky base such as potassium tert-butoxide in tert-butyl alcohol, the less substituted alkene is formed as the major product.

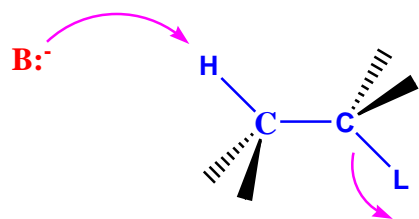


The reasons for this behaviour seem to be related partly to the steric bulk of the base and to the fact that in tert-butyl alcohol the base is associated with solvent molecules and thus made even larger. Because of the greater crowding at the internal (secondary) hydrogen atoms, the large tert-butoxide ion appears to have difficulty in removing it in the transition state so it removes one of the more exposed primary hydrogen atoms of the methyl group instead. When an elimination reaction yields the less substituted alkene the reaction is said to follow Hofmann rule.

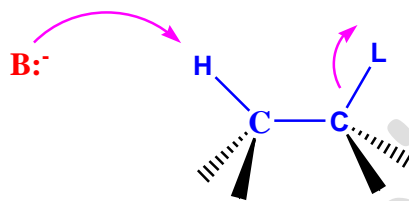
The Stereochemistry of E2 Reactions: The Orientation of Groups in The Transition State

Considerable experimental evidence indicates that the five atoms involved in the transition state of an E2 reaction including the base must lie in the same plane. The coplanarity of the H-C-C-L

unit is necessary for proper overlap of the orbitals in the developing Pi bond of the alkene being formed. There are two ways that this can happen.



**Anti periplanar transition state
(Preferred)**



Syn periplanar transition state

Evidence also indicates that the arrangement called the anti periplanar conformation is the preferred one. The syn periplanar transition state occurs only with rigid molecules that are unable to assume the anti arrangement. Anti periplanar transition state is staggered and therefore of lower energy while the syn periplanar transition state is eclipsed.