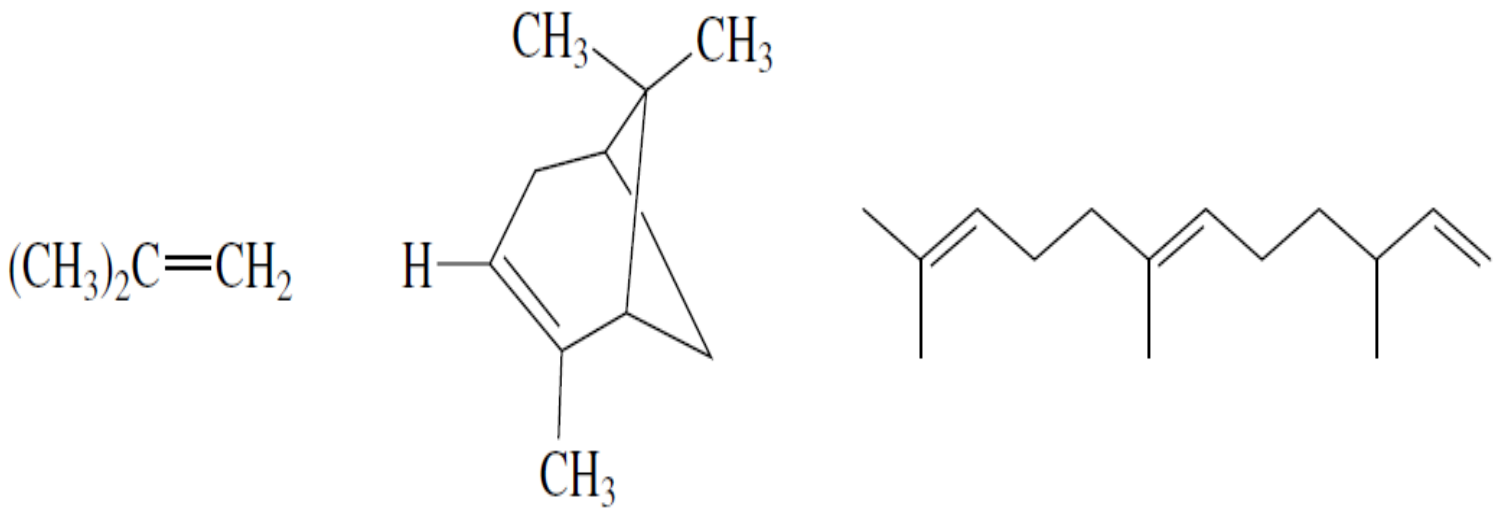
Alkenes

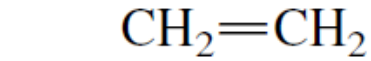


Isobutylene
(used in the production of synthetic rubber)

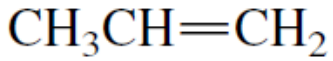
α-Pinene
(a major constituent of turpentine)

Farnesene
(present in the waxy coating found on apple skins)

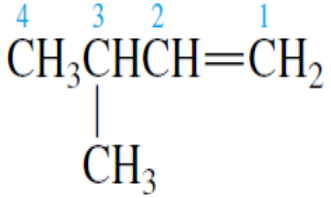
Nomenclature



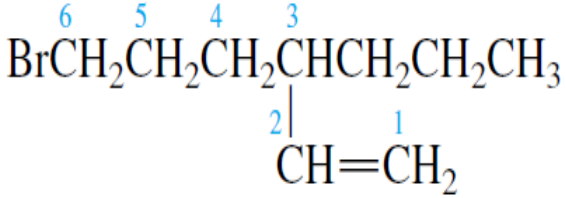
IUPAC name: **ethene**
Common name: ethylene



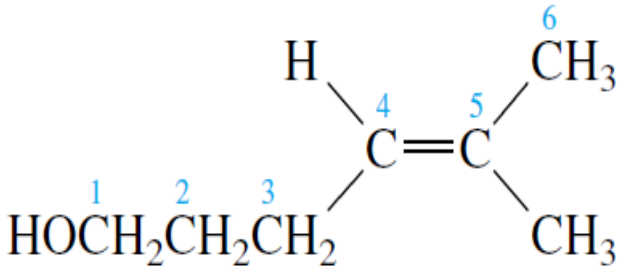
IUPAC name: **propene**
Common name: propylene



3-Methyl-1-butene
(not 2-methyl-3-butene)



6-Bromo-3-propyl-1-hexene
(longest chain that contains double bond is six carbons)



5-Methyl-4-hexen-1-ol
(not 2-methyl-2-hexen-6-ol)

Alkenyl groups

$CH_2{=}CH{-}$ as in $CH_2{=}CHCl$

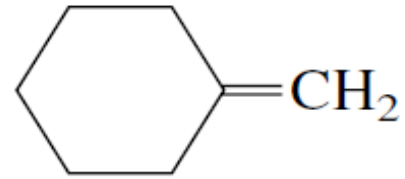
Vinyl — Vinyl chloride

$CH_2{=}CHCH_2{-}$ as in $CH_2{=}CHCH_2OH$

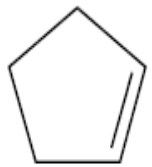
Allyl — Allyl alcohol

$CH_2{=}C(CH_3){-}$ as in $CH_2{=}CCl(CH_3)$

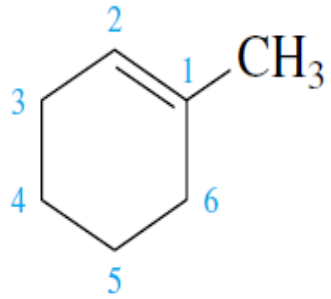
Isopropenyl — Isopropenyl chloride



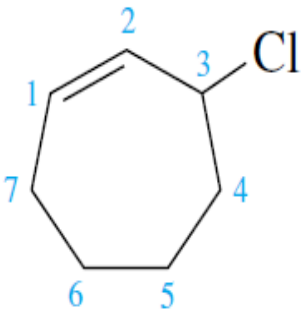
Methylenecyclohexane



Cyclopentene

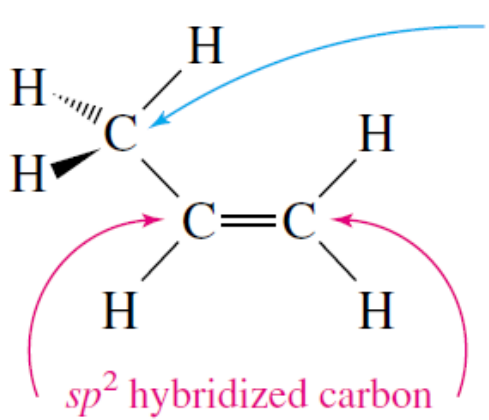


1-Methylcyclohexene

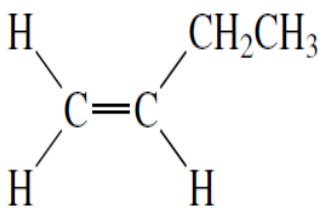


3-Chlorocycloheptene

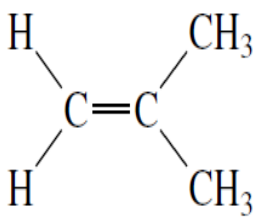
(not 1-chloro-2-cycloheptene)



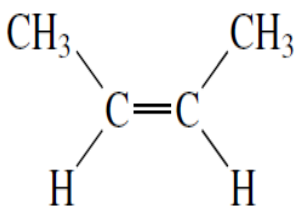
C—C bond length = 150 pm
C=C bond length = 134 pm



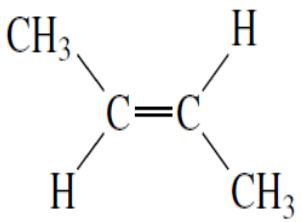
1-Butene



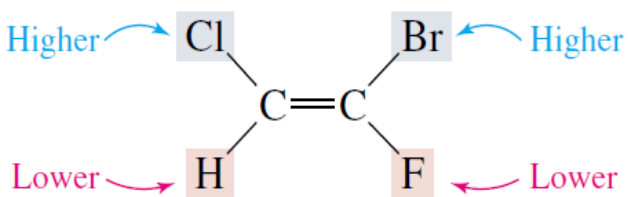
2-Methylpropene



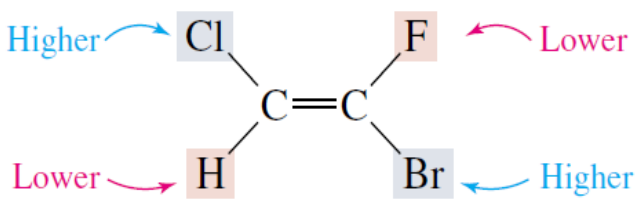
cis-2-Butene



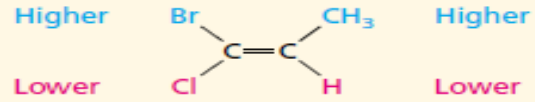
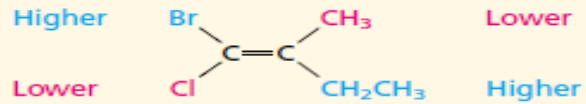
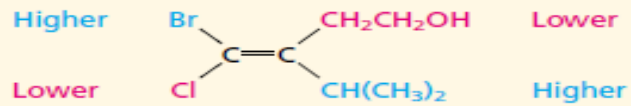
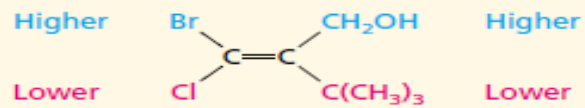
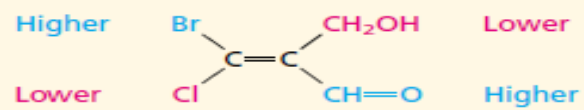
trans-2-Butene

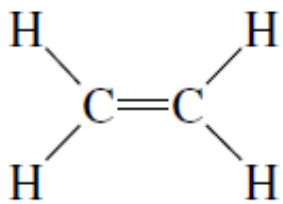


Z configuration
Higher ranked substituents (Cl and Br) are on same side of double bond

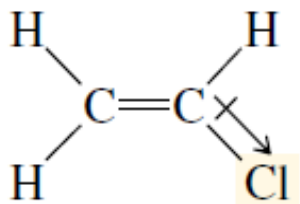


E configuration
Higher ranked substituents (Cl and Br) are on opposite sides of double bond

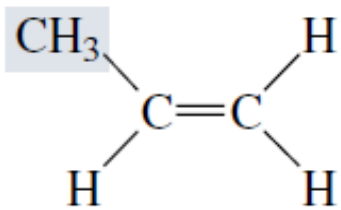
Rule	Example
1. Higher atomic number takes precedence over lower. Bromine (atomic number 35) outranks chlorine (atomic number 17). Methyl (C, atomic number 6) outranks hydrogen (atomic number 1).	The compound  has the *Z* configuration. Higher ranked atoms (Br and C of CH_3) are on the same side of the double bond.
2. When two atoms directly attached to the double bond are identical, compare the atoms attached with these two on the basis of their atomic numbers. Precedence is determined at the first point of difference: Ethyl [—C(C,H,H)] outranks methyl [—C(H,H,H)] Similarly, *tert*-butyl outranks isopropyl, and isopropyl outranks ethyl: $—C(CH_3)_3 > —CH(CH_3)_2 > —CH_2CH_3$ —C(C,C,C) > —C(C,C,H) > —C(C,H,H)	The compound  has the *E* configuration.
3. Work outward from the point of attachment, comparing all the atoms attached to a particular atom before proceeding further along the chain: $—CH(CH_3)_2$ [—C(C,C,H)] outranks $—CH_2CH_2OH$ [—C(C,H,H)]	The compound  has the *E* configuration.
4. When working outward from the point of attachment, always evaluate substituent atoms one by one, never as a group. Since oxygen has a higher atomic number than carbon, $—CH_2OH$ [—C(O,H,H)] outranks $—C(CH_3)_3$ [—C(C,C,C)]	The compound  has the *Z* configuration.
5. An atom that is multiply bonded to another atom is considered to be replicated as a substituent on that atom: —CH(=O) is treated as if it were —C(O,O,H) The group —CH=O [—C(O,O,H)] outranks $—CH_2OH$ [—C(O,H,H)]	The compound  has the *E* configuration.



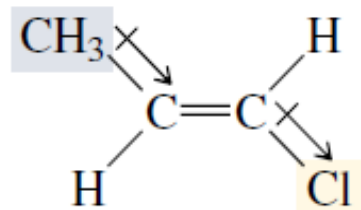
Ethylene
$\mu = 0$ D



Chloroethene
$\mu = 1.4$ D

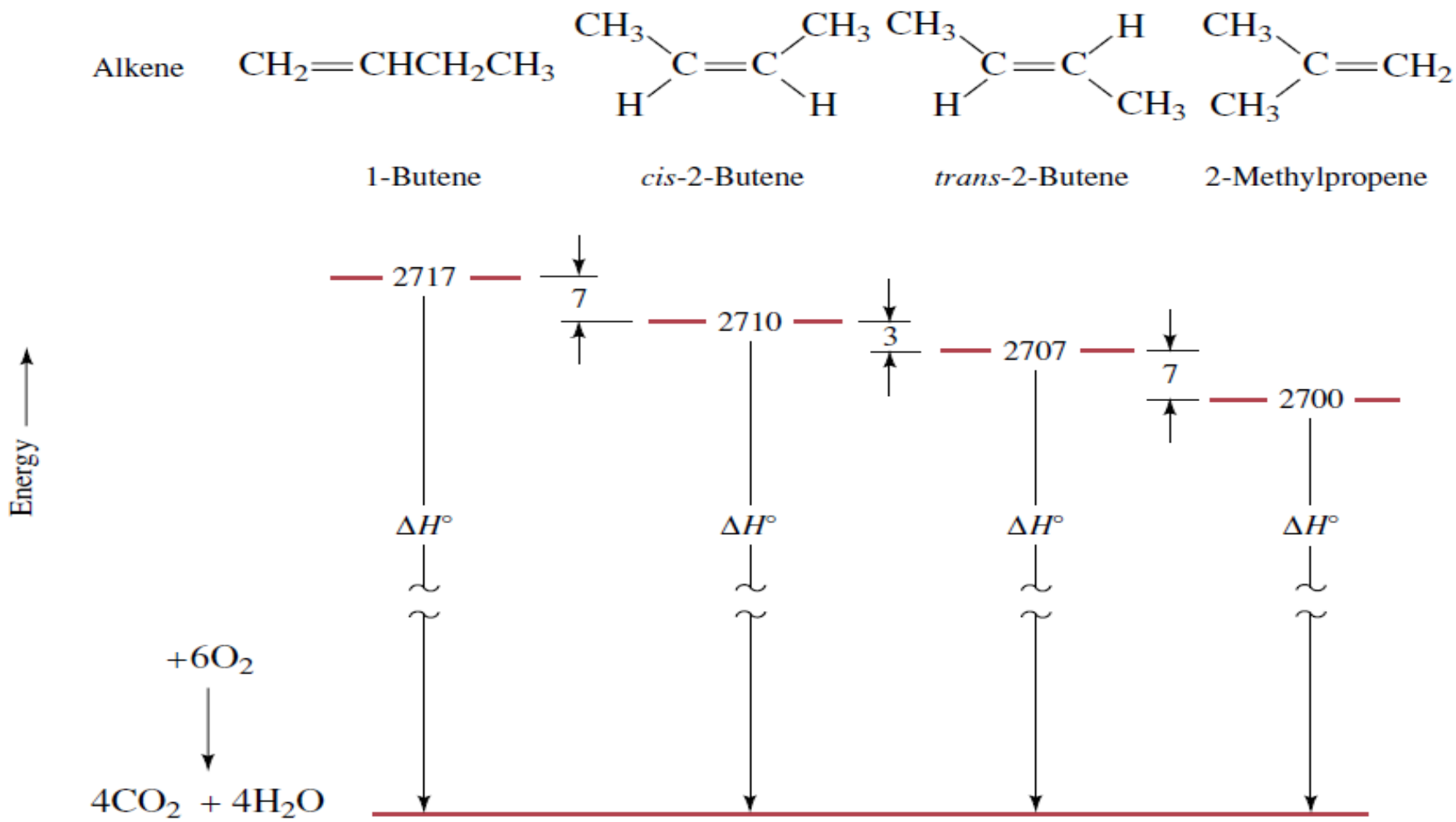


Propene
$\mu = 0.3$ D

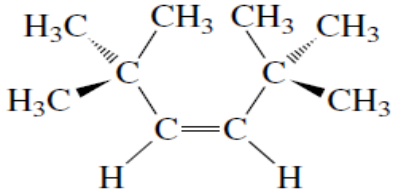


trans-1-Chloropropene
$\mu = 1.7$ D

Relative stability of alkenes

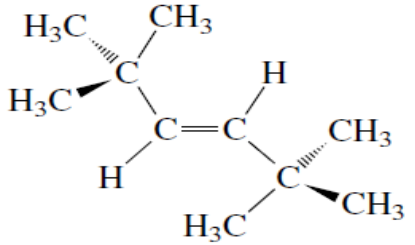


Heat of combustion

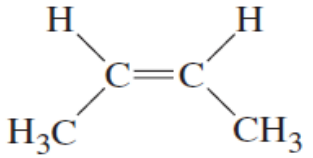


cis-2,2,5,5-Tetramethyl-3-hexene
Less stable

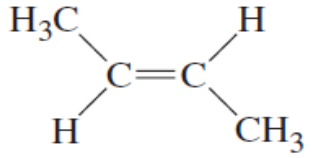
Energy difference =
44 kJ/mol
(10.5 kcal/mol)



trans-2,2,5,5-Tetramethyl-3-hexene
More stable

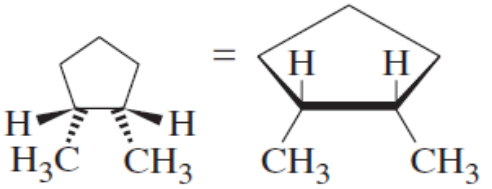


cis-but-2-ene

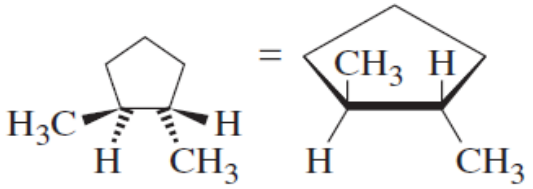


trans-but-2-ene

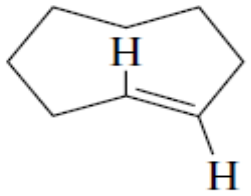
Cis-trans isomerization



cis-1,2-dimethylcyclopentane

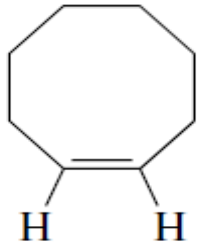


trans-1,2-dimethylcyclopentane



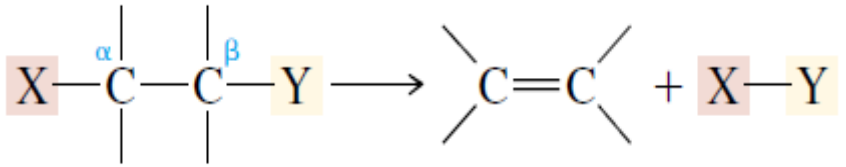
(*E*)-Cyclooctene
(*trans*-cyclooctene)
Less stable

Energy difference =
39 kJ/mol (9.2 kcal/mol)

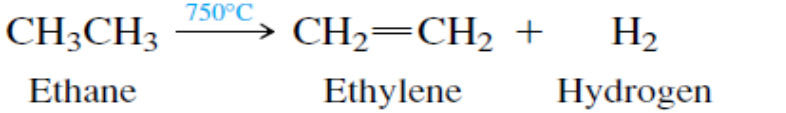


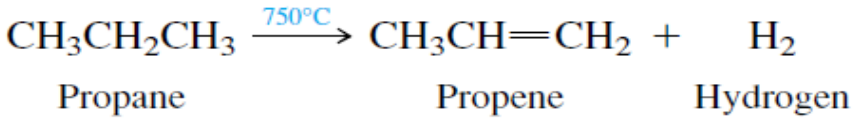
(*Z*)-Cyclooctene
(*cis*-cyclooctene)
More stable

Preparation of alkenes:

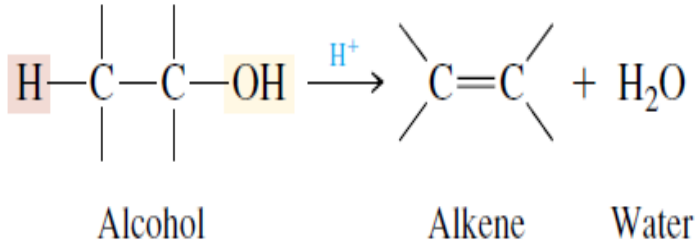


Dehydrogention of alkanes:

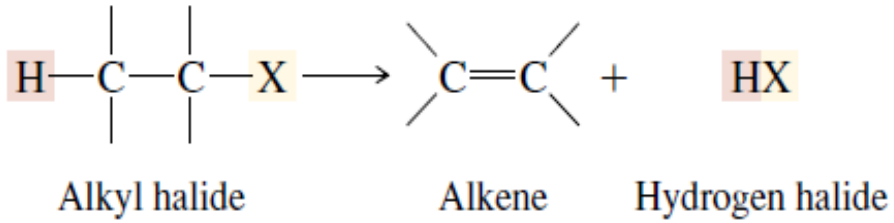




Dehydration of alcohols:



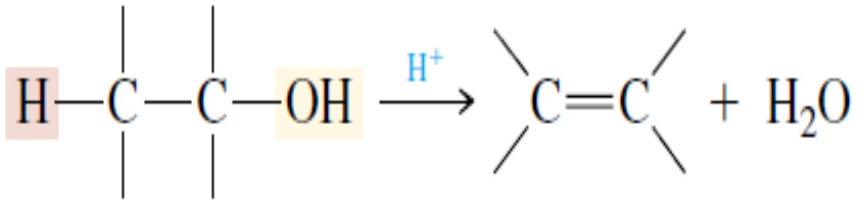
Dehydrohalogenation of alkyl halides:



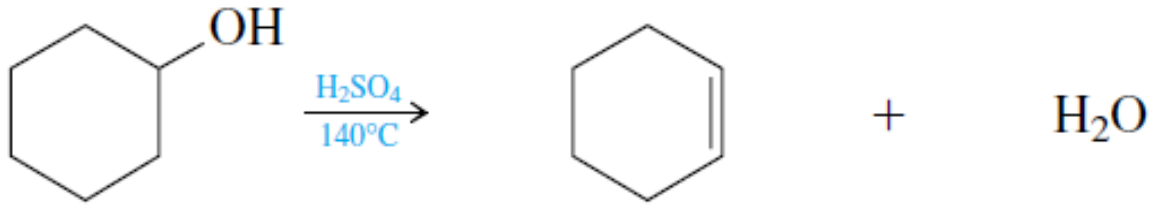
$$CH_3CH_2OH \xrightarrow[160^\circ C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

Ethyl alcohol — Ethylene — Water

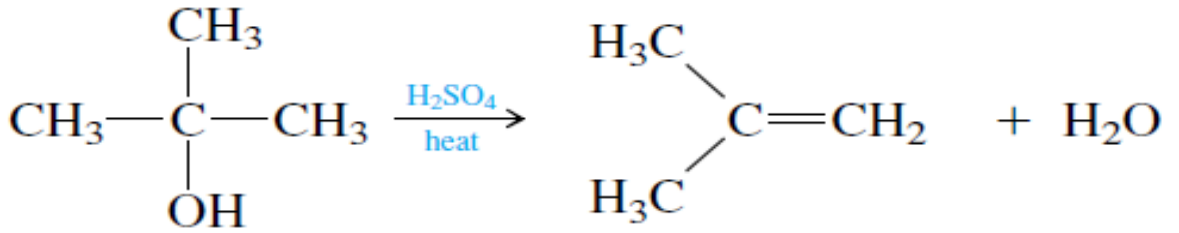
Dehydration of alcohols:



Alcohol — Alkene — Water

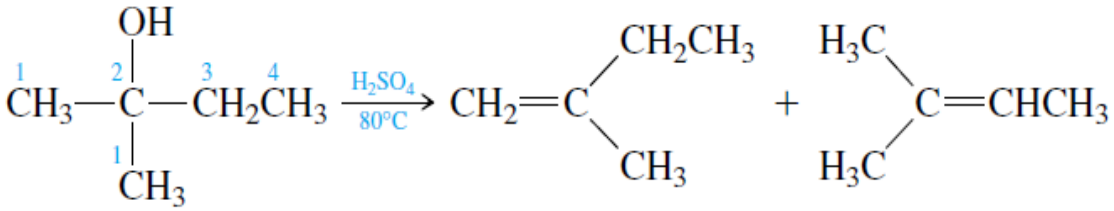


Cyclohexanol — Cyclohexene (79–87%) — Water



2-Methyl-2-propanol — 2-Methylpropene (82%) — Water

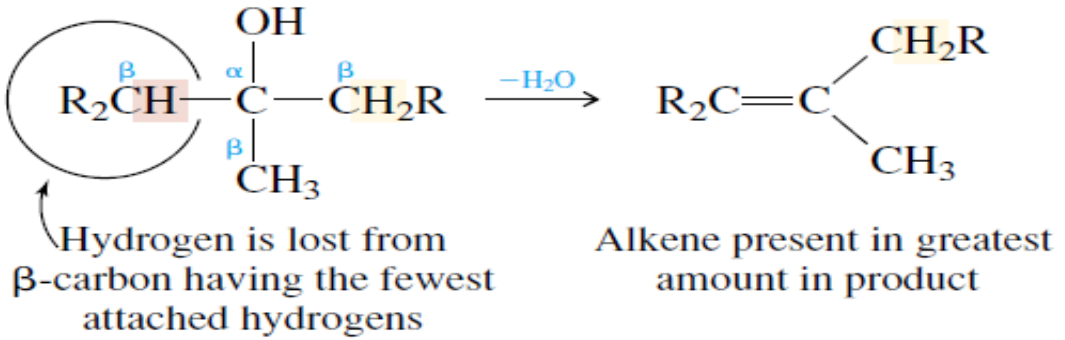
Regioselectivity-Syetzef rule

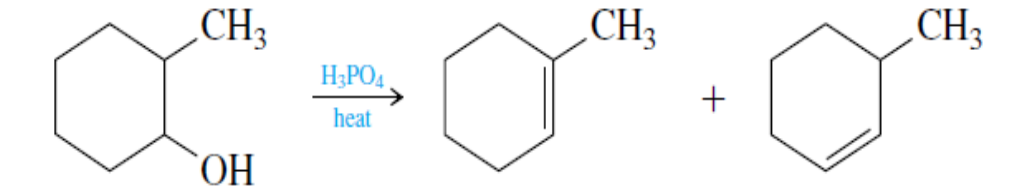


2-Methyl-2-butanol

2-Methyl-1-butene (10%)

2-Methyl-2-butene (90%)

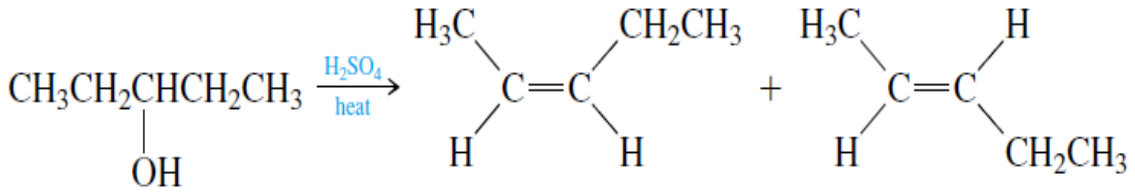




2-Methylcyclohexanol

1-Methylcyclohexene (84%)

3-Methylcyclohexene (16%)



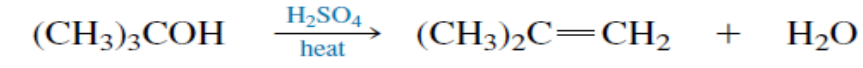
3-Pentanol

cis-2-Pentene (25%) (minor product)

trans-2-Pentene (75%) (major product)

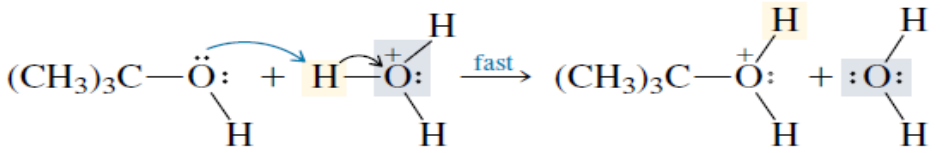
Mechanism

The overall reaction:



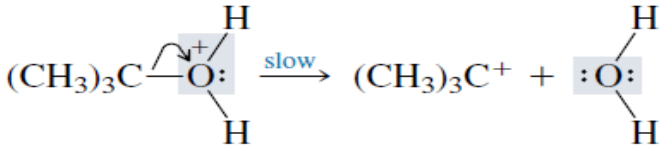
tert-Butyl alcohol — 2-Methylpropene — Water

Step (1): Protonation of *tert*-butyl alcohol.



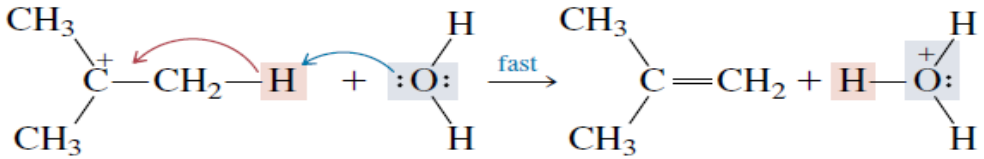
tert-Butyl alcohol — Hydronium ion — *tert*-Butyloxonium ion — Water

Step (2): Dissociation of *tert*-butyloxonium ion.

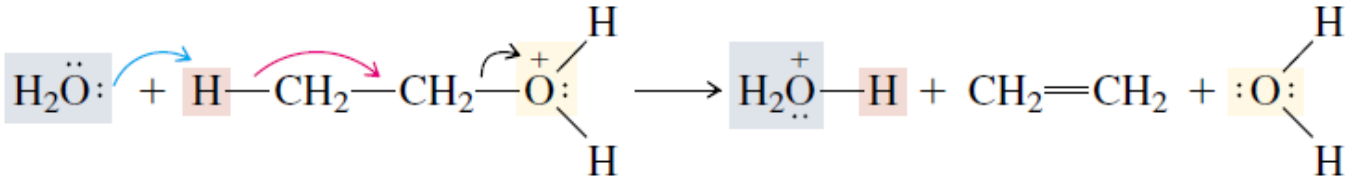


tert-Butyloxonium ion — *tert*-Butyl cation — Water

Step (3): Deprotonation of *tert*-butyl cation

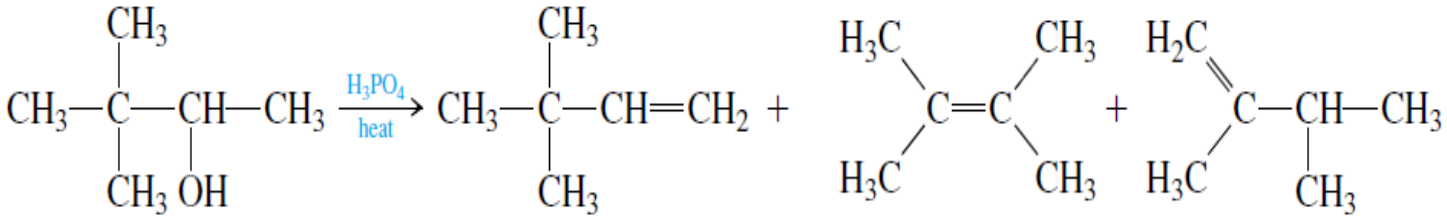


tert-Butyl cation — Water — 2-Methylpropene — Hydronium ion

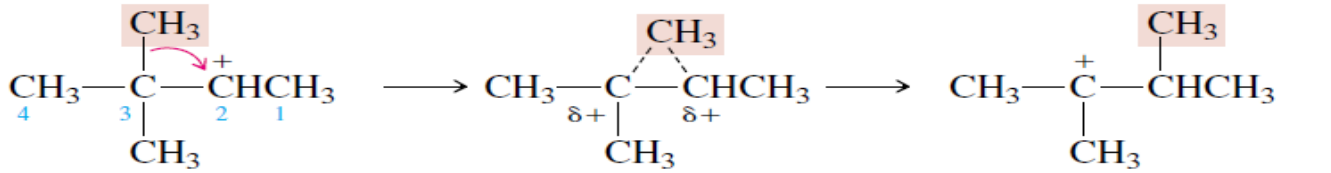


Water | Ethyloxonium ion | Hydronium ion | Ethylene | Water

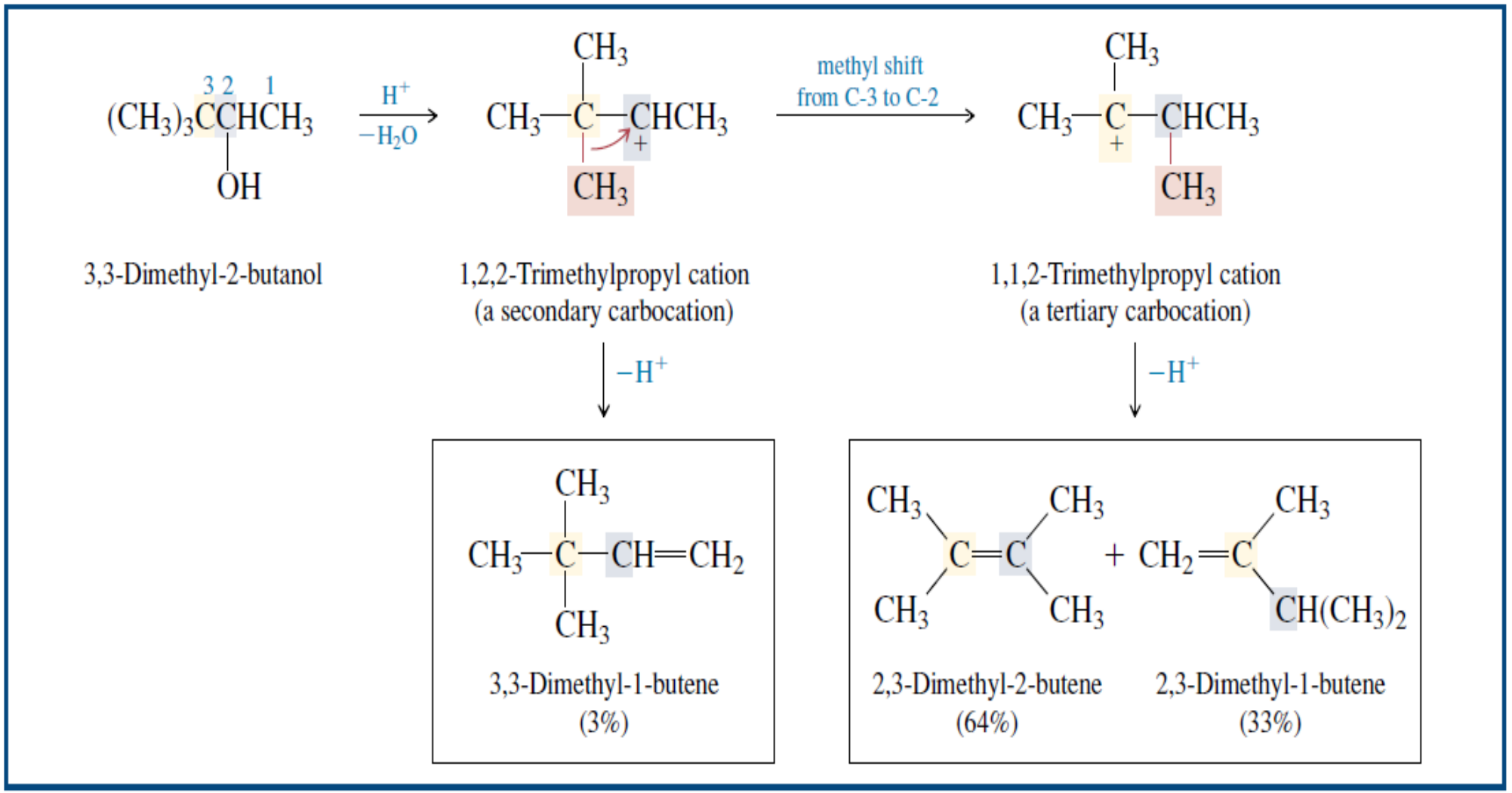
Rearrangement

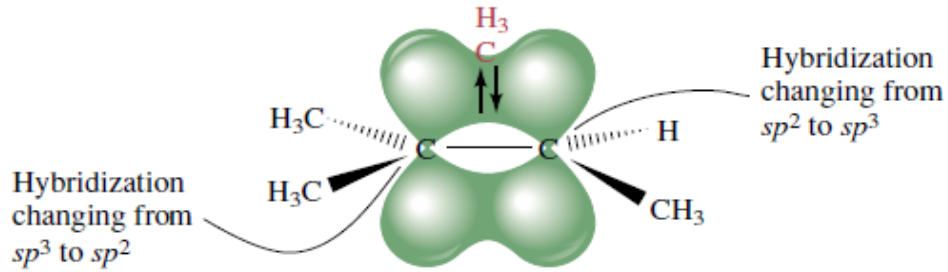


3,3-Dimethyl-2-butanol | 3,3-Dimethyl-1-butene (3%) | 2,3-Dimethyl-2-butene (64%) | 2,3-Dimethyl-1-butene (33%)

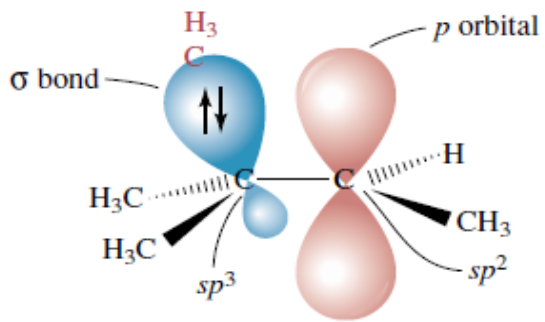


1,2,2-Trimethylpropyl cation (secondary, less stable) | Transition state for methyl migration (dashed lines indicate partial bonds) | 1,1,2-Trimethylpropyl cation (tertiary, more stable)


3 2 1
(CH3)3CCHCH3
OH
H+
−H2O
CH3
CH3—C—CHCH3
+
CH3
methyl shift
from C-3 to C-2
CH3
CH3—C—CHCH3
+
CH3
3,3-Dimethyl-2-butanol
1,2,2-Trimethylpropyl cation
(a secondary carbocation)
1,1,2-Trimethylpropyl cation
(a tertiary carbocation)
−H+
−H+
CH3
CH3—C—CH=CH2
CH3
3,3-Dimethyl-1-butene
(3%)
CH3
CH3
C=C
CH3
CH3
+
CH3
CH2=C
CH(CH3)2
2,3-Dimethyl-2-butene
(64%)
2,3-Dimethyl-1-butene
(33%)

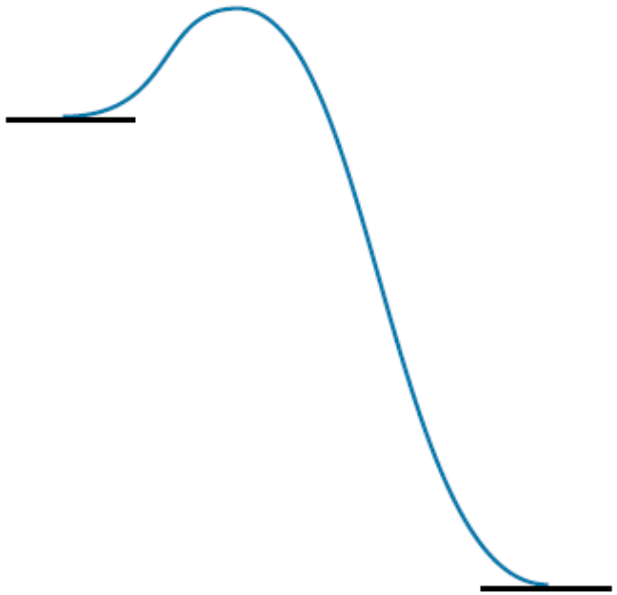


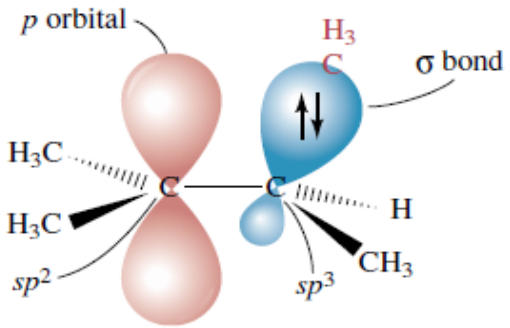
(*b*)



(*a*)

1,2,2-Trimethylpropyl cation
(secondary)

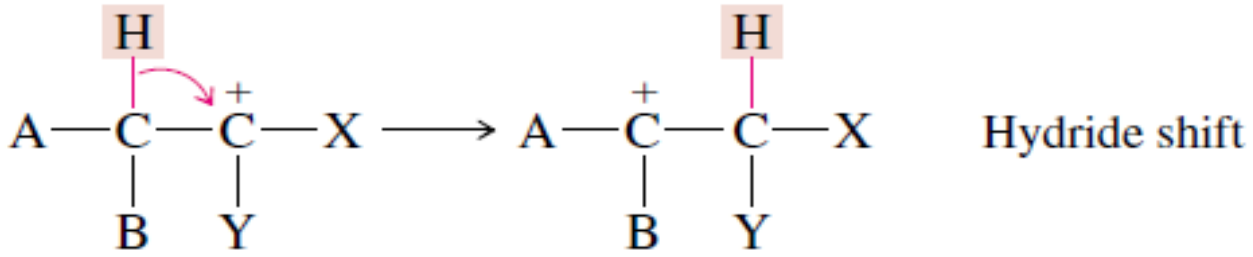




(*c*)

1,1,2-Trimethylpropyl cation
(tertiary)

Hydride shift

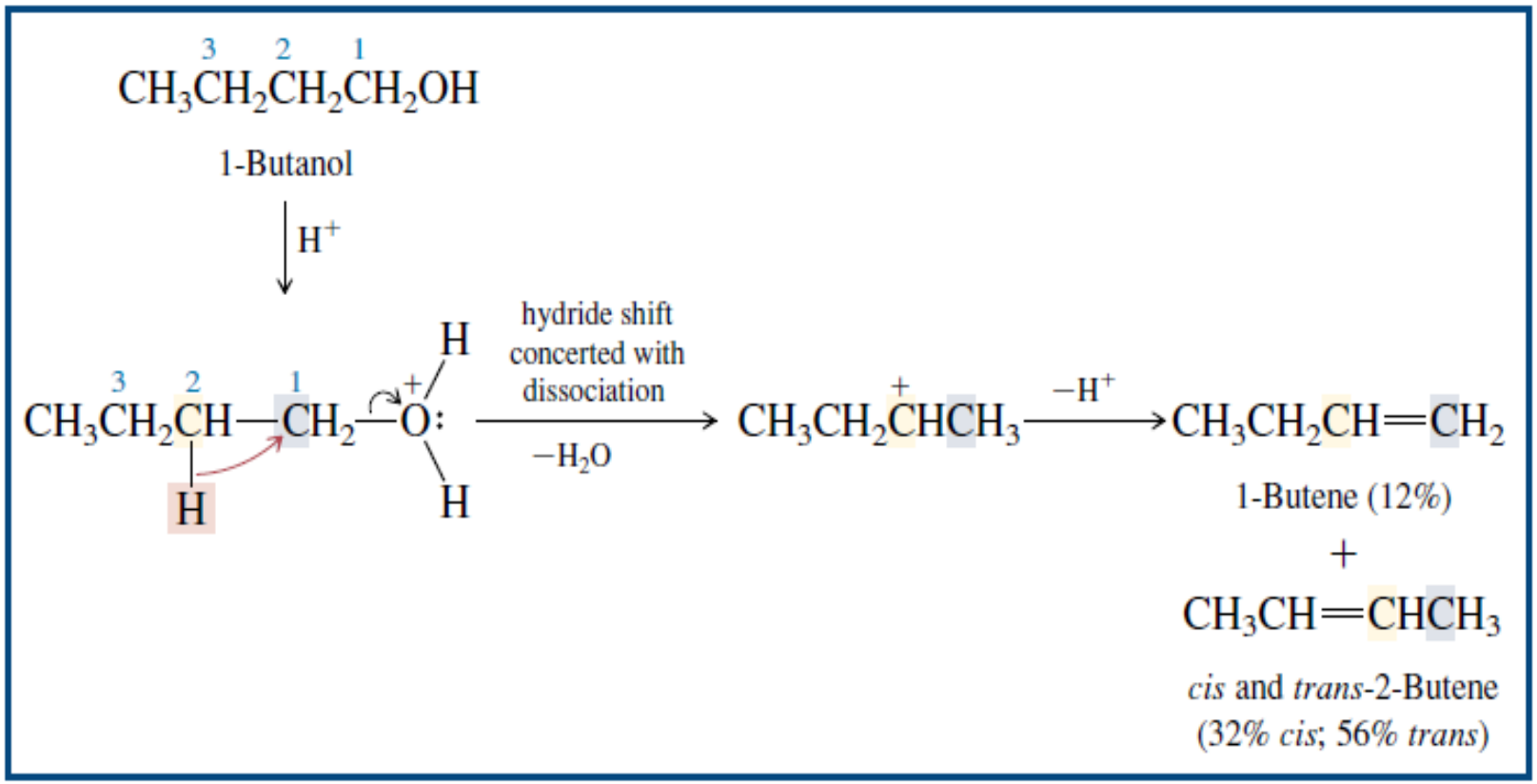


Hydride shift

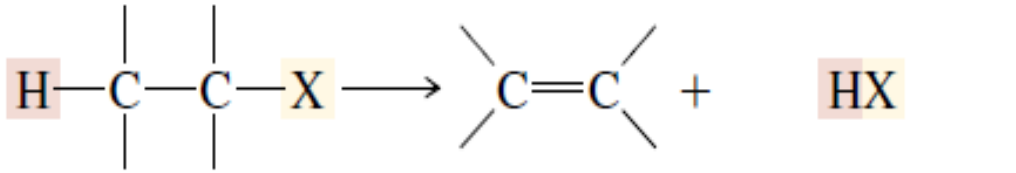
$$CH_3CH_2CH_2CH_2OH \xrightarrow[140\text{–}170^\circ C]{H_2SO_4} CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3$$

1-Butene (12%)

Mixture of *cis*-2-butene (32%) and *trans*-2-butene (56%)

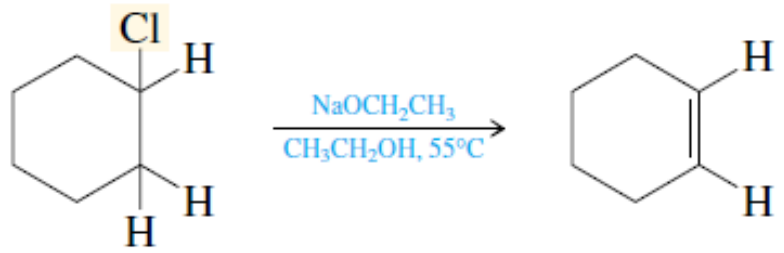

3 2 1
CH3CH2CH2CH2OH
1-Butanol
H+
hydride shift
concerted with
dissociation
−H2O
−H+
CH3CH2CH=CH2
1-Butene (12%)
+
CH3CH=CHCH3
cis and trans-2-Butene
(32% cis; 56% trans)

Dehydrohalogenation of alkyl halides

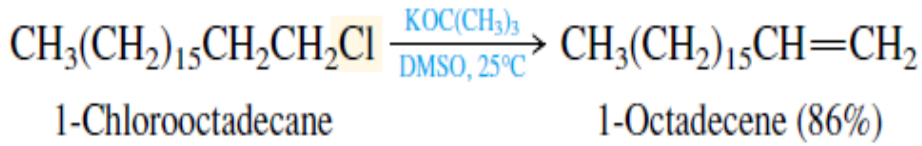


Alkyl halide Alkene Hydrogen halide

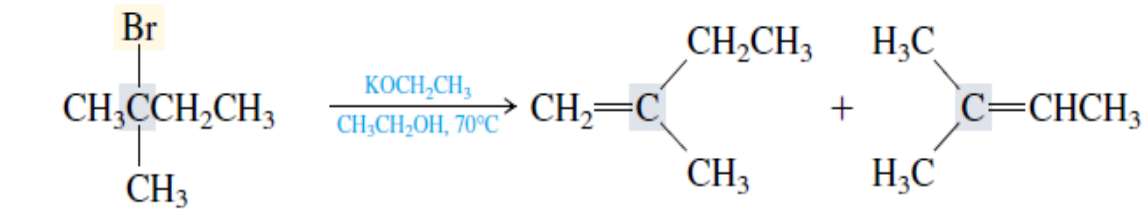
Alkyl halide Sodium ethoxide Alkene Ethyl alcohol Sodium halide



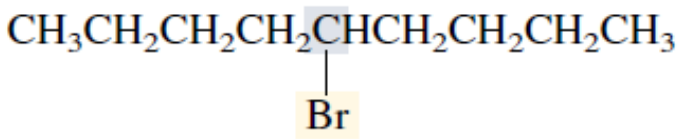
Cyclohexyl chloride Cyclohexene (100%)



1-Chlorooctadecane — 1-Octadecene (86%)

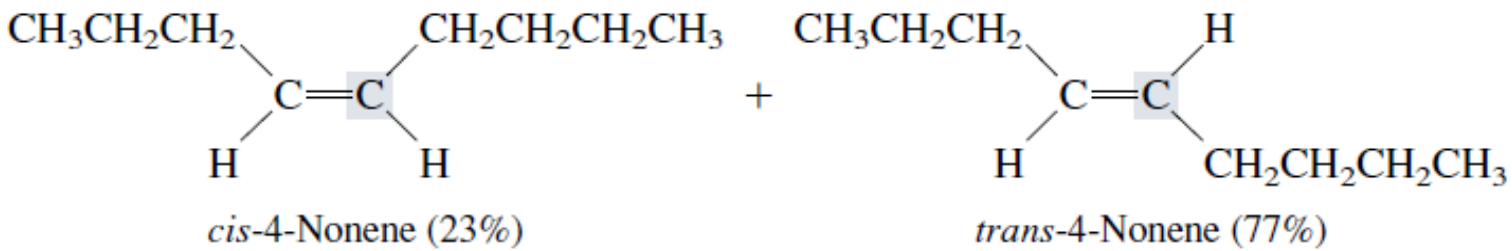


2-Bromo-2-methylbutane — 2-Methyl-1-butene (29%) + 2-Methyl-2-butene (71%)

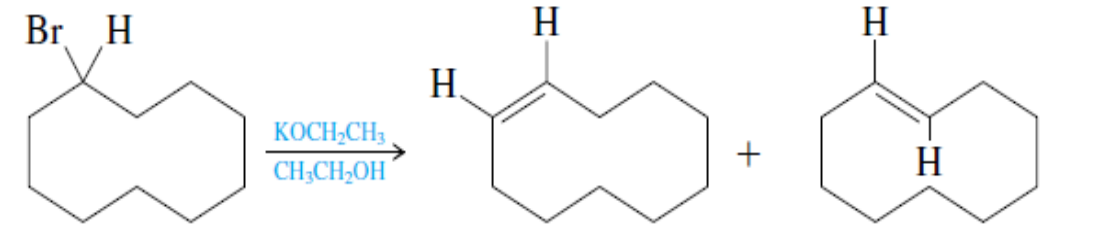


5-Bromononane

KOCH2CH3, CH3CH2OH



cis-4-Nonene (23%) + *trans*-4-Nonene (77%)



Bromocyclodecane

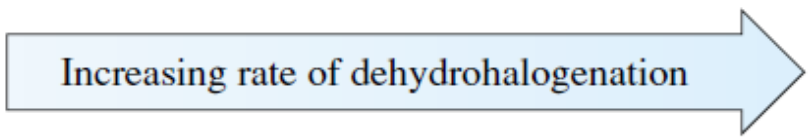
cis-Cyclodecene
[(Z)-cyclodecene] (85%)

trans-Cyclodecene
[(*E*)-cyclodecene] (15%)

1. *The reaction exhibits second-order kinetics; it is first-order in alkyl halide and first-order in base.*

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

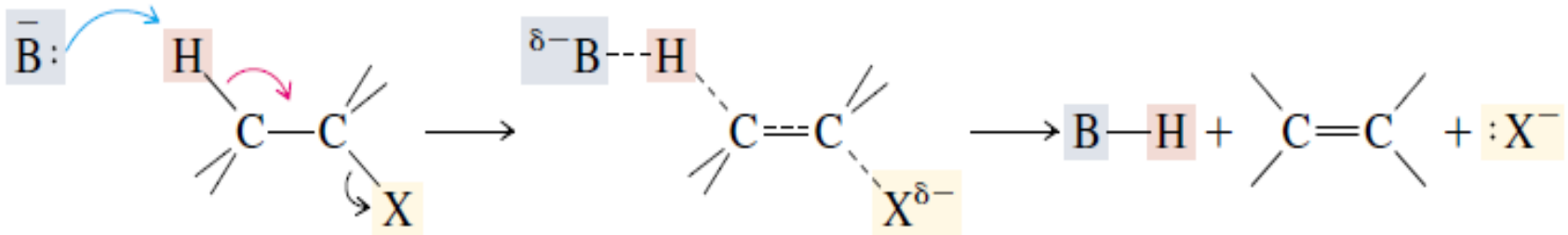
2. *The rate of elimination depends on the halogen, the reactivity of alkyl halides increasing with decreasing strength of the carbon–halogen bond.*



RF < RCl < RBr < RI

Alkyl fluoride
(slowest rate of elimination;
strongest carbon–halogen bond)

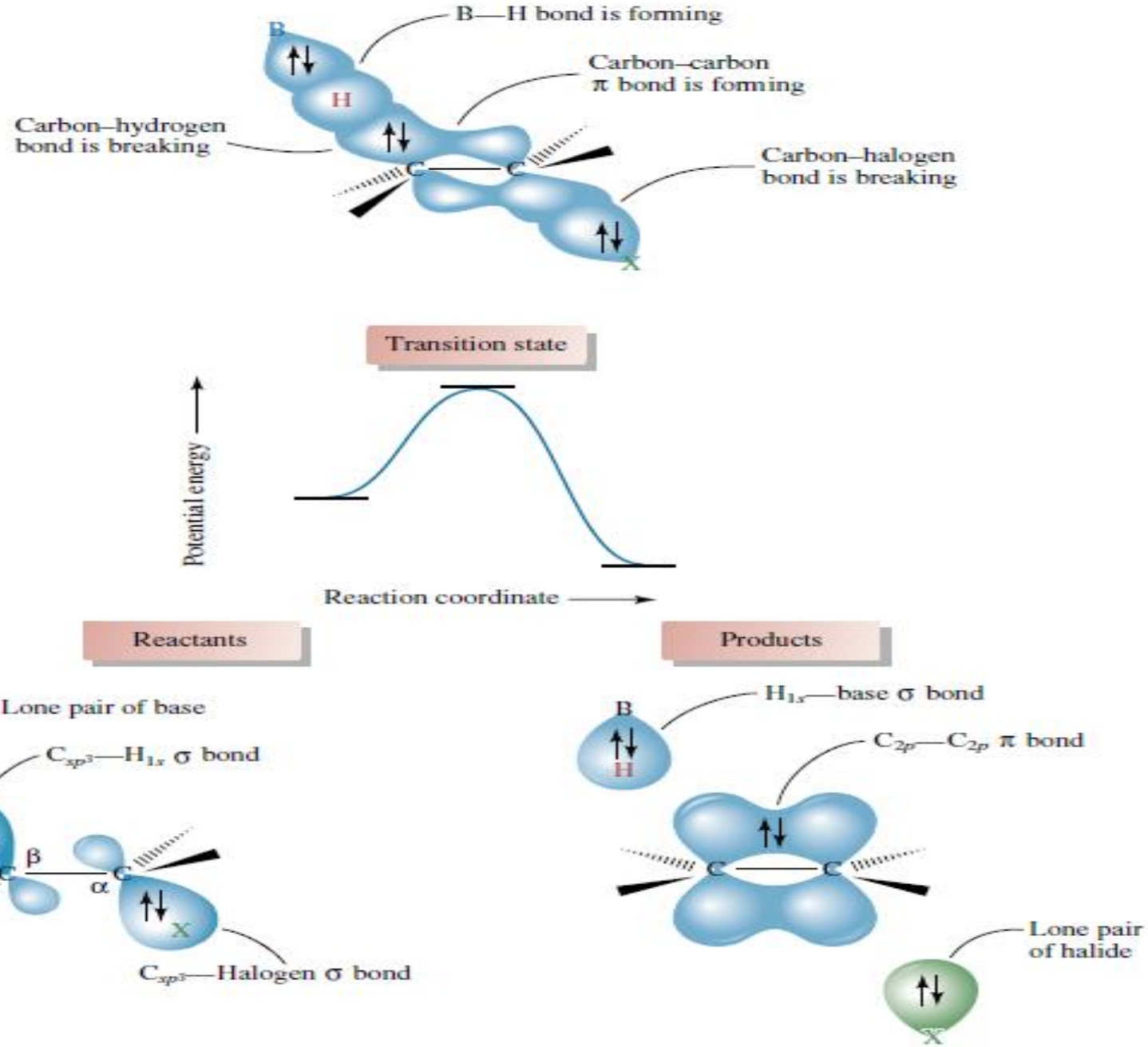
Alkyl iodide
(fastest rate of elimination;
weakest carbon–halogen bond)

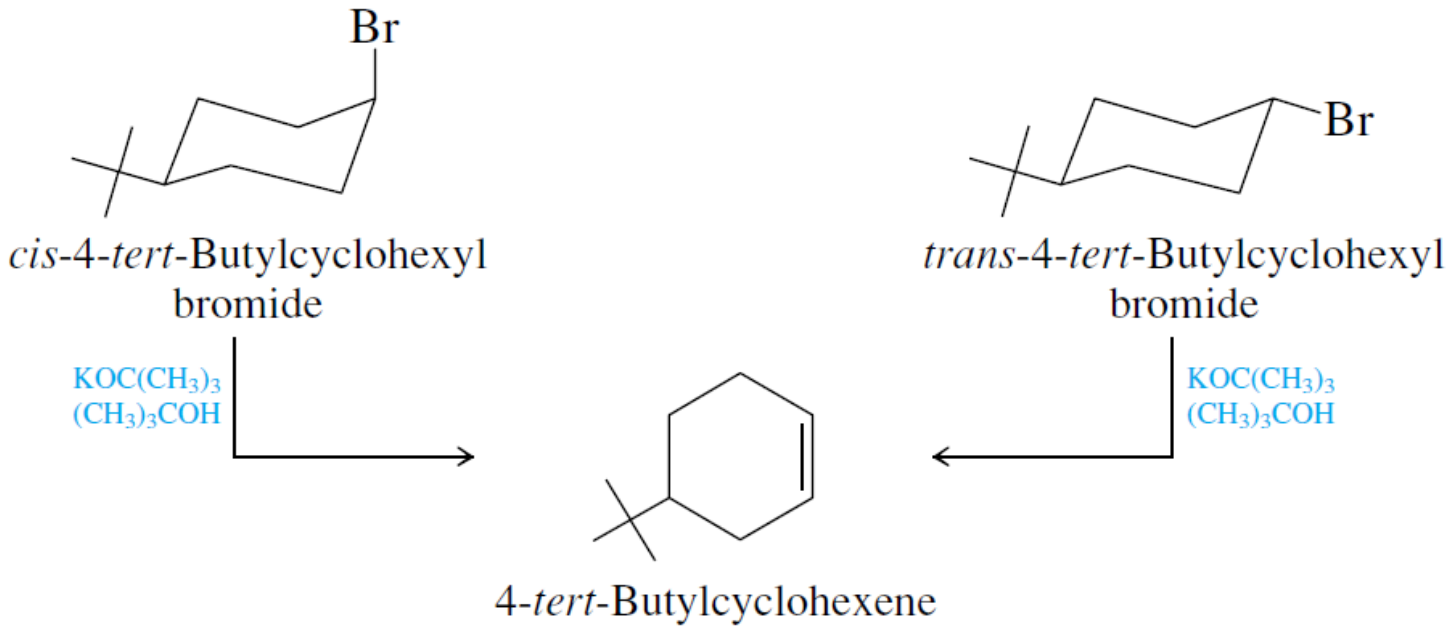


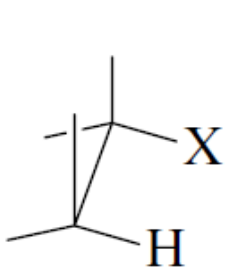
Transition state for bimolecular elimination

In the E2 mechanism the three key elements

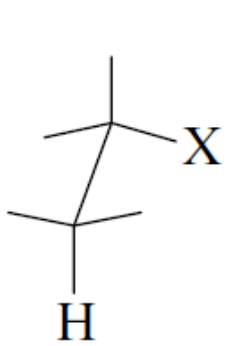
1. C—H bond breaking
2. C=C π bond formation
3. C—X bond breaking


B—H bond is forming
Carbon–carbon
π bond is forming
Carbon–hydrogen
bond is breaking
Carbon–halogen
bond is breaking
Transition state
Potential energy
Reaction coordinate
Reactants
Products
Lone pair of base
C_{sp^3}—H_{1s} σ bond
β
α
C_{sp^3}—Halogen σ bond
H_{1s}—base σ bond
C_{2p}—C_{2p} π bond
Lone pair
of halide

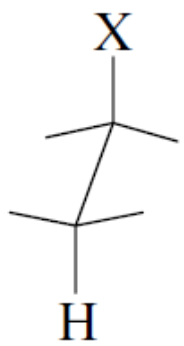




Syn periplanar; orbitals aligned but bonds are eclipsed



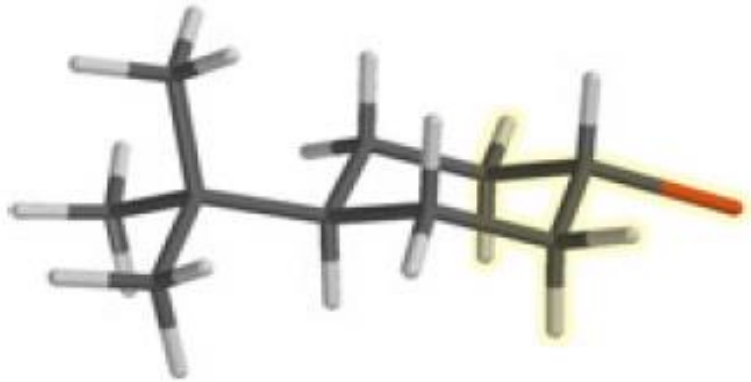
Gauche; orbitals not aligned for double bond formation



Anti periplanar; orbitals aligned and bonds are staggered

cis-4-*tert*-Butylcyclohexyl bromide

Axial halide is in proper orientation for anti elimination with respect to axial hydrogens on adjacent carbon atoms.
Dehydrobromination is rapid.



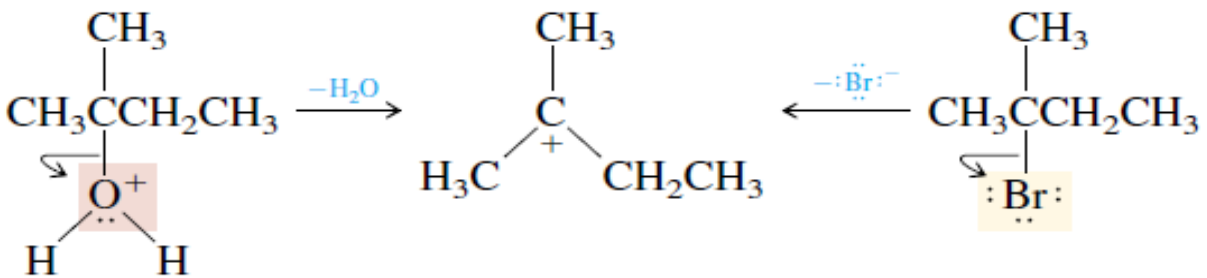
trans-4-*tert*-Butylcyclohexyl bromide

Equatorial halide is gauche to axial and equatorial hydrogens on adjacent carbon; cannot undergo anti elimination in this conformation.
Dehydrobromination is slow.

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

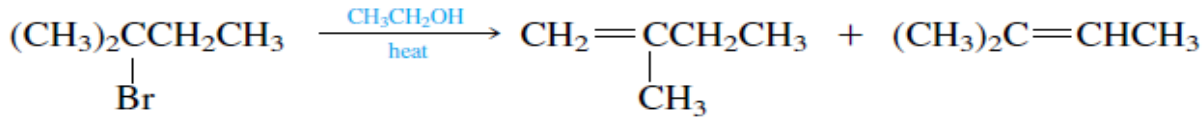
Increasing rate of elimination by the E1 mechanism

RCH_2X	<	R_2CHX	<	R_3CX
Primary alkyl halide slowest rate of E1 elimination				Tertiary alkyl halide fastest rate of E1 elimination



Alkyloxonium ion | Carbocation | Alkyl halide

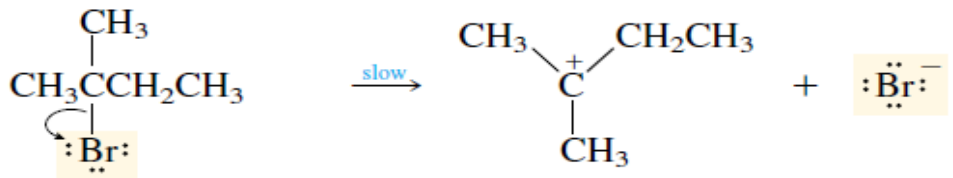
The reaction:



2-Bromo-2-methylbutane — 2-Methyl-1-butene (25%) — 2-Methyl-2-butene (75%)

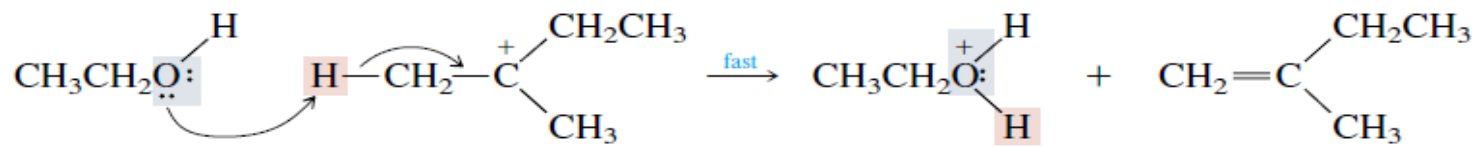
The mechanism:

Step (1): Alkyl halide dissociates by heterolytic cleavage of carbon–halogen bond. (Ionization step)

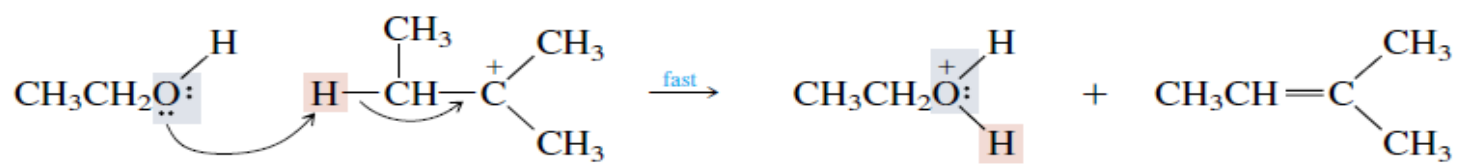


2-Bromo-2-methylbutane — 1,1-Dimethylpropyl cation — Bromide ion

Step (2): Ethanol acts as a base to remove a proton from the carbocation to give the alkene products. (Deprotonation step)



Ethanol — 1,1-Dimethylpropyl cation — Ethyloxonium ion — 2-Methyl-1-butene



Ethanol — 1,1-Dimethylpropyl cation — Ethyloxonium ion — 2-Methyl-2-butene