# Reactions Of Alkenes Via Protonation

from chapter(s) _____ in the recommended text

## A. Introduction

## B. Protonation Of Alkenes

### Generation Of Carbocations Via Protonation

*simplest*

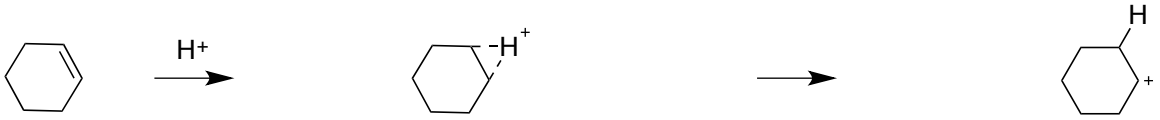
*sp*$^3$ hybridized carbon and a *sp*$^2$

*transition*

*intermediate*.

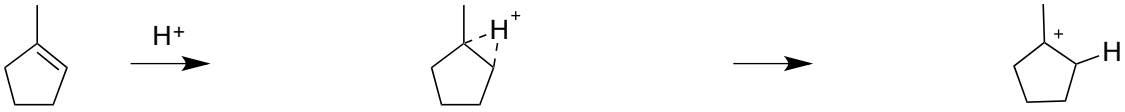

*protonated alkene*
*transition state*

*carbonium ion*
*intermediate*




*protonated alkene*
*transition state*

*carbonium ion*
*intermediate*



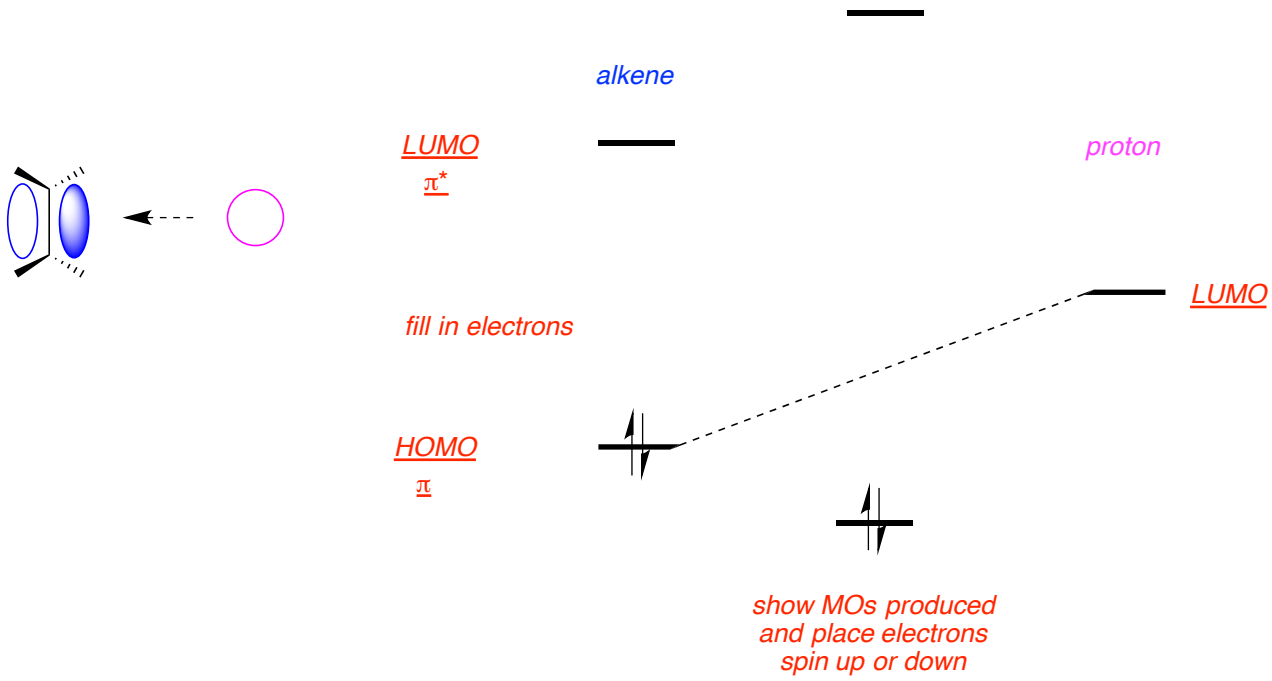

*protonated alkene*
*transition state*

*carbonium ion*
*intermediate*

$sp^3$ hybridized carbon and $sp^2$

## A Molecular Orbital Picture Of Alkene Protonation

*more*
*does not*
*LUMO*
*LUMO*
*HOMO*



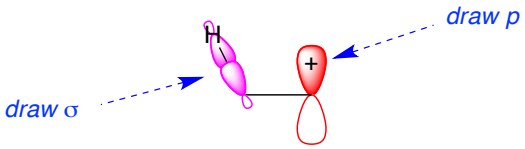

*stabilizing*.

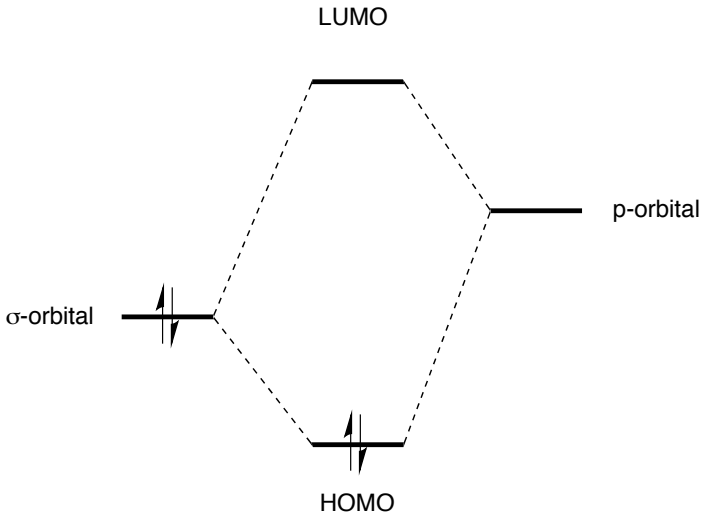
## C. Carbocation Stabilities

*alternative theories to explain bonding in general*.

(*LUMO*)

methyl (*HOMO*




*2* electrons into the interaction, whereas the p-orbital bears *0*

2_

*are in the same plane*.

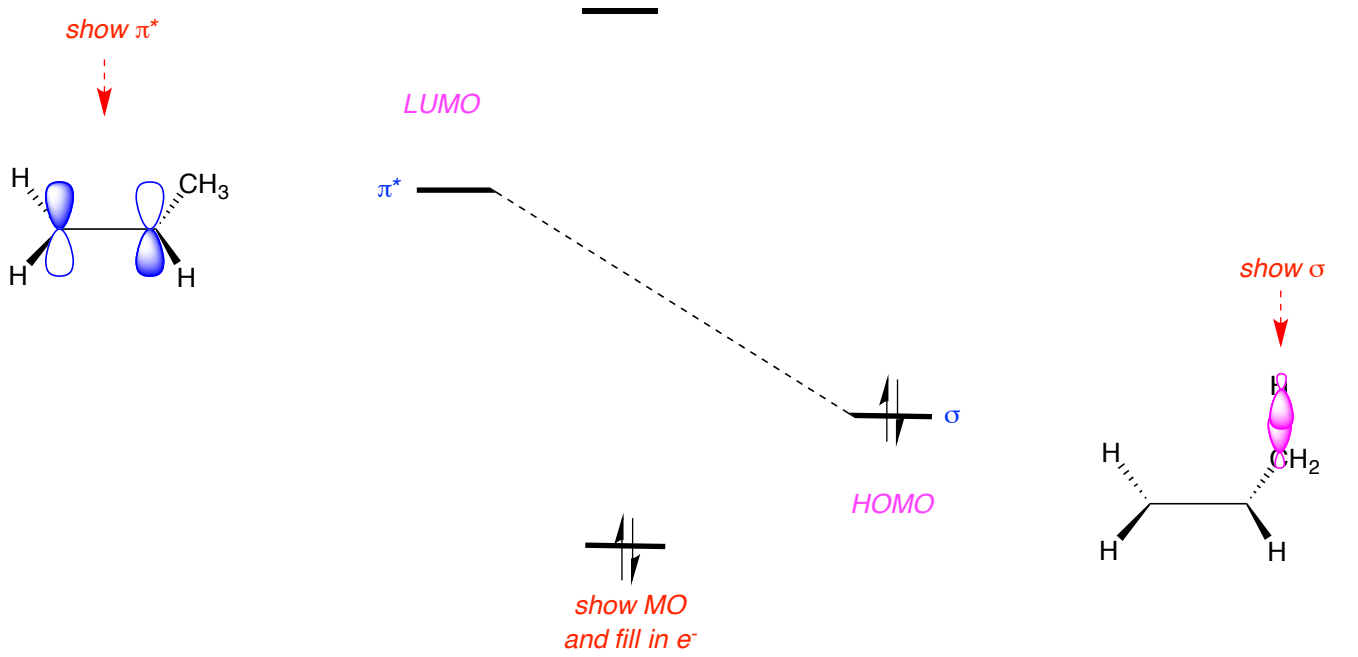
*cannot achieve significant orbital overlap*.

*2* adjacent methyl groups, and therefore *2* *more*

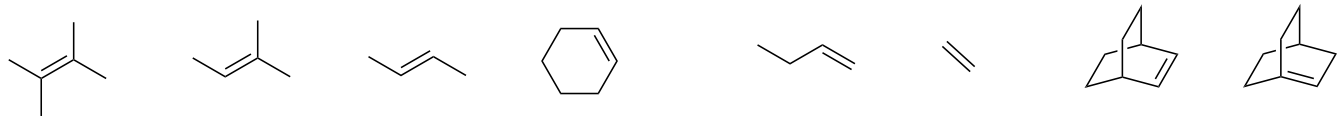
*3* adjacent methyl groups, and therefore *3* *more*

## D. Alkenes Stabilities

*increase with*



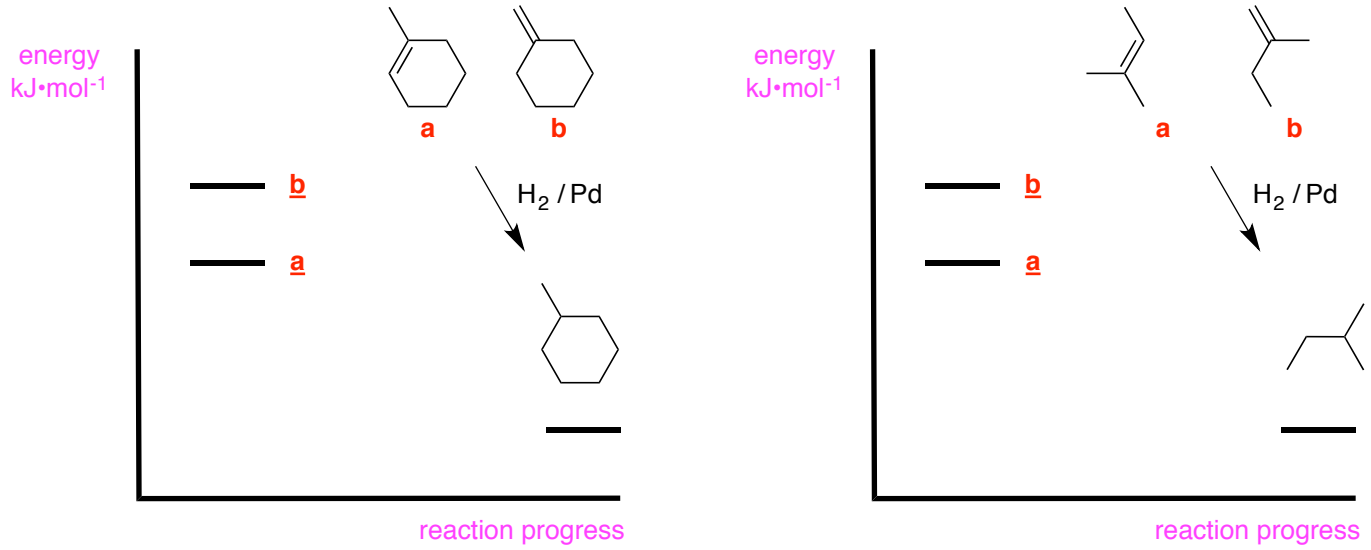

*stabilizing*
*enhanced*



*most stable* *least stable*

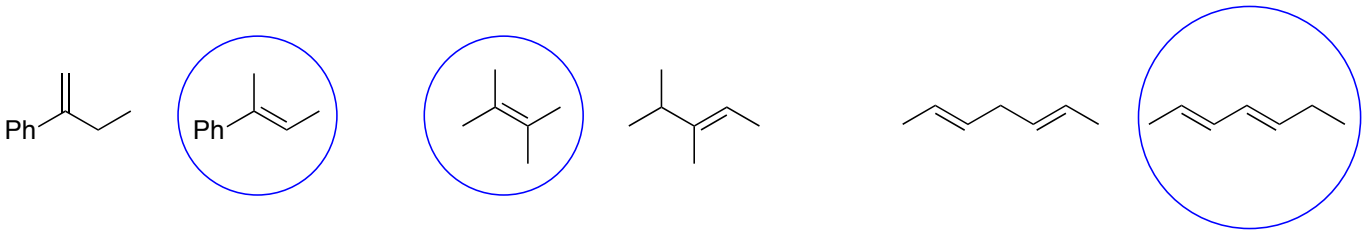
### Heats Of Hydrogenation

Energy is *liberated*
*lower*
*can*
*hydrogenation*.

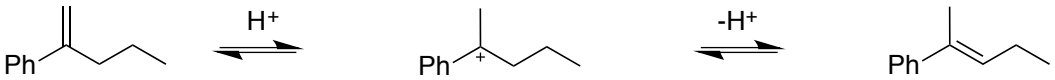



*b*
the right it is *b*.

## E. Acid-mediated Alkene Isomerization

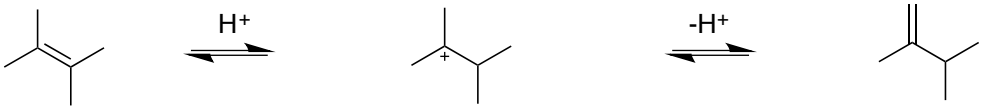



*is* an isomer of the first.
*thermodynamics*.



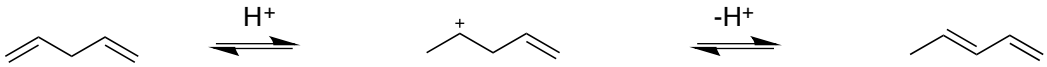

*K* = *≥1*

carbocation alkene




*K* = *≤1*

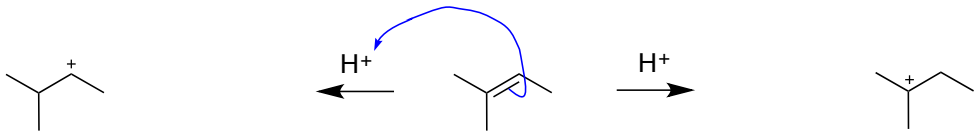
carbocation alkene




*K* = *≥1*

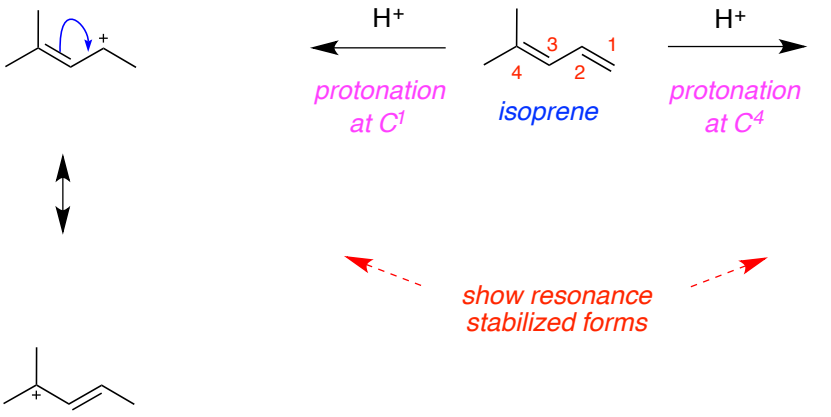
carbocation alkene

It is *conceivable*




*least favorable*
*2° carbonium ion*

*most favorable*
*3° carbonium ion*




*protonation at C¹*

*isoprene*

*protonation at C⁴*

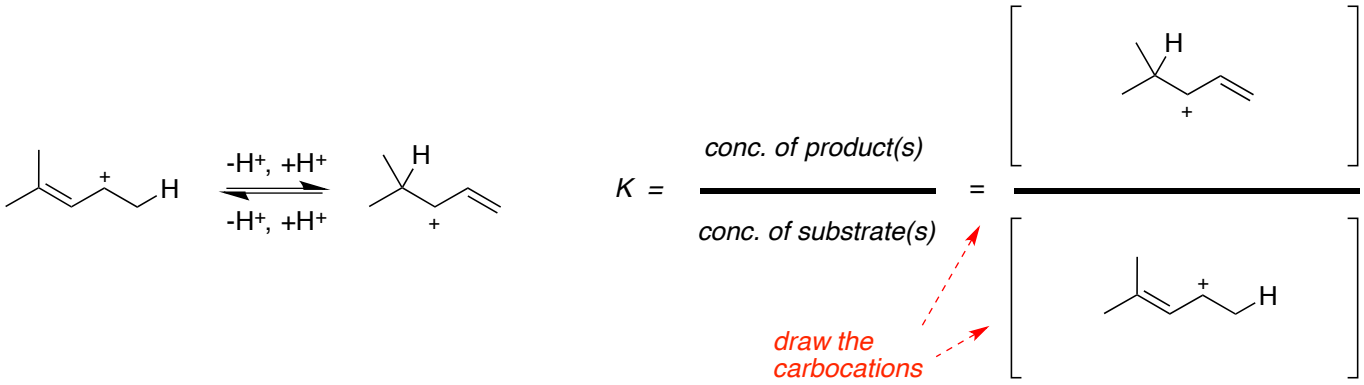
*show resonance stabilized forms*

*most favorable*
*3° carbonium ion*

*least favorable*
*1° carbonium ion*

*gives*
*does not*.

*small*
*equals*




less than one.

## F. Carbocation Rearrangements

### Hydride Shifts

hydride

hydride anion.

: true.

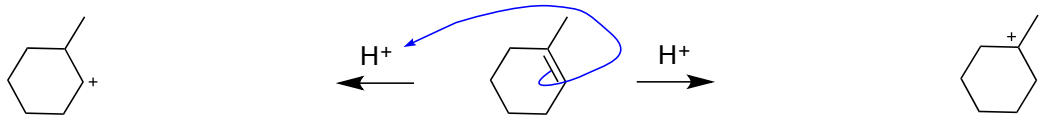
1,2-hydride



may

*most*

*intermediates*




*least favorable*
*2° carbonium ion*

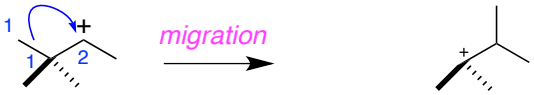
*most favorable*
*3° carbonium ion*

## Alkyl Shifts

*opposite*
*more*
*secondary / tertiary*
*tertiary*

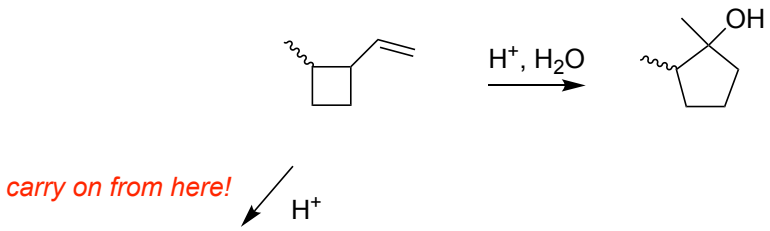
*1,2-*


*draw curly arrows*



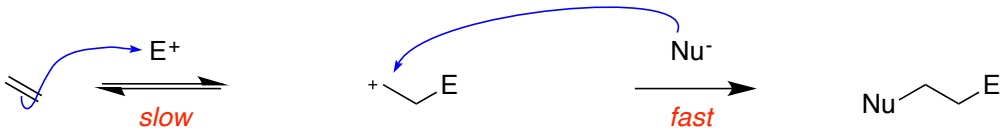

*draw curly arrows*
*and product*


*alkyl shift*
*most* able
*less* stable than $Et^+$.



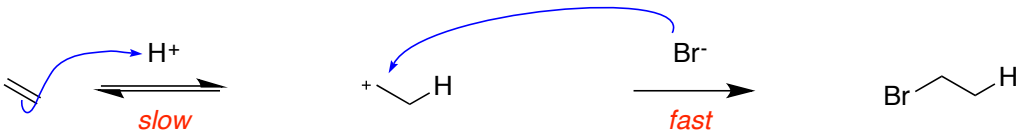

see: https://youtu.be/FsQb6o510EY

## G. Electrophilic Addition Mechanisms



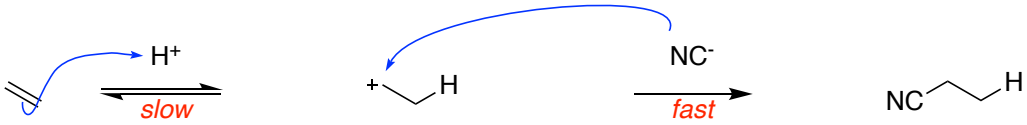

*carbocation intermediate* *addition product*

*slow*



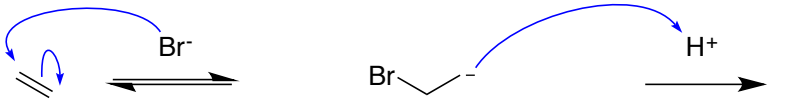

carbocation intermediate

addition product




carbocation intermediate

addition product



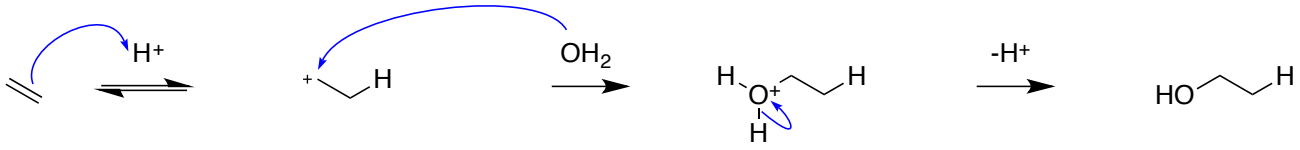

carbanion intermediate

addition product

*does not* proceed

- bromide, being negatively charged, is repelled by electrons in the alkene π-bond

*proton*,




*carbocation intermediate* | *protonated addition product* | *hydration product*

## H. Acid-mediated Hydration Of Alkenes

*1°*.

*two*

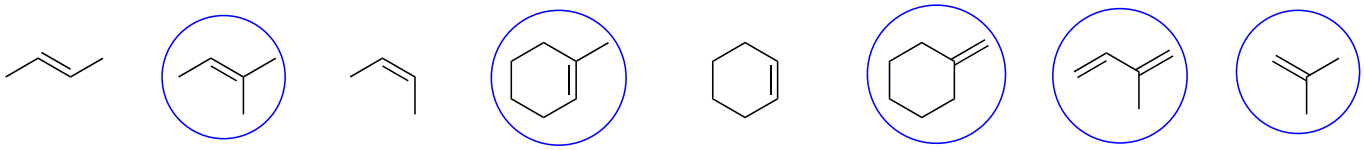
*ie* *regioisomers*;


*2-propanol* | *1-propanol*

*regioselective*.

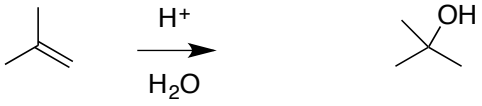
, reactions that involve reaction of one chemical functional group in preference to others are called *chemoselective*.

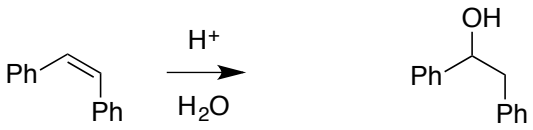
*enantioselective* and *diastereoselective*



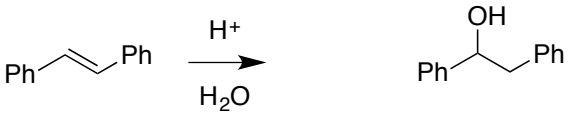
*gives 2-propanol*
*more stable*

*gives 1-propanol*
*less stable*



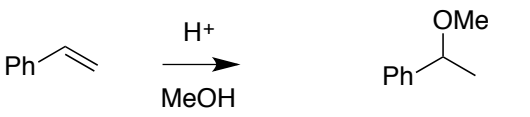



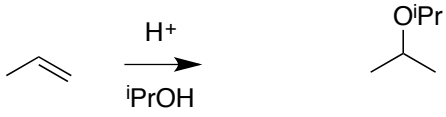





*E1* pathway.

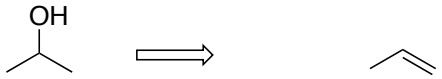
*ethers*.

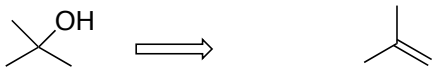


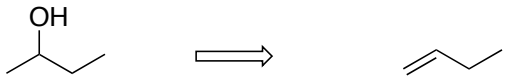



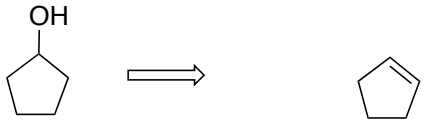


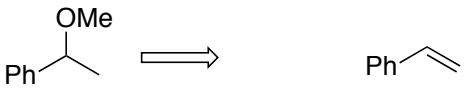

*are not*

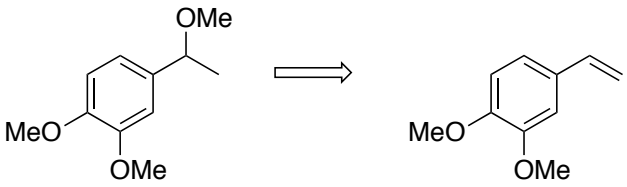

OH

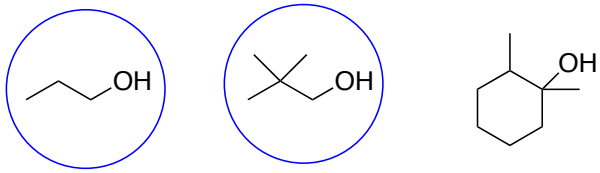

OH

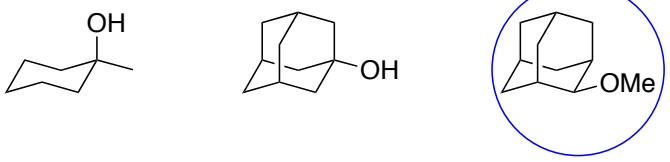

OH


OH


OMe
Ph
Ph


OMe
MeO
OMe
MeO
OMe


OH
OH
OH


OH
OH
OMe