Objective 10

Apply Reactivity Principles to Elimination Reactions:
identify structural features (alpha C, H on beta C, LG)
Use curved arrows to predict product.
Compare E1 vs. E2 mechanisms.

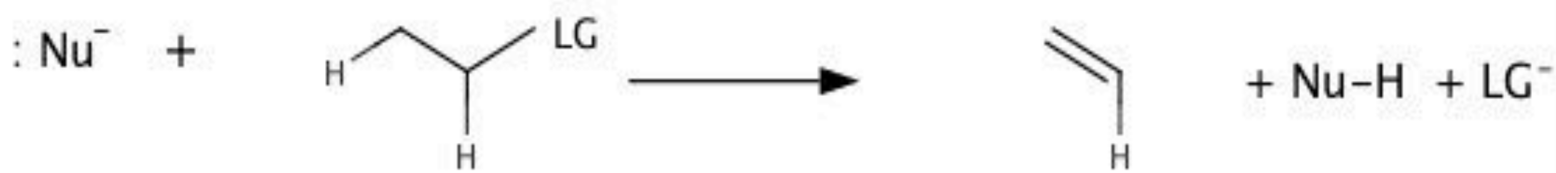
4 Types of Organic Polar Reactions

Acid–Base

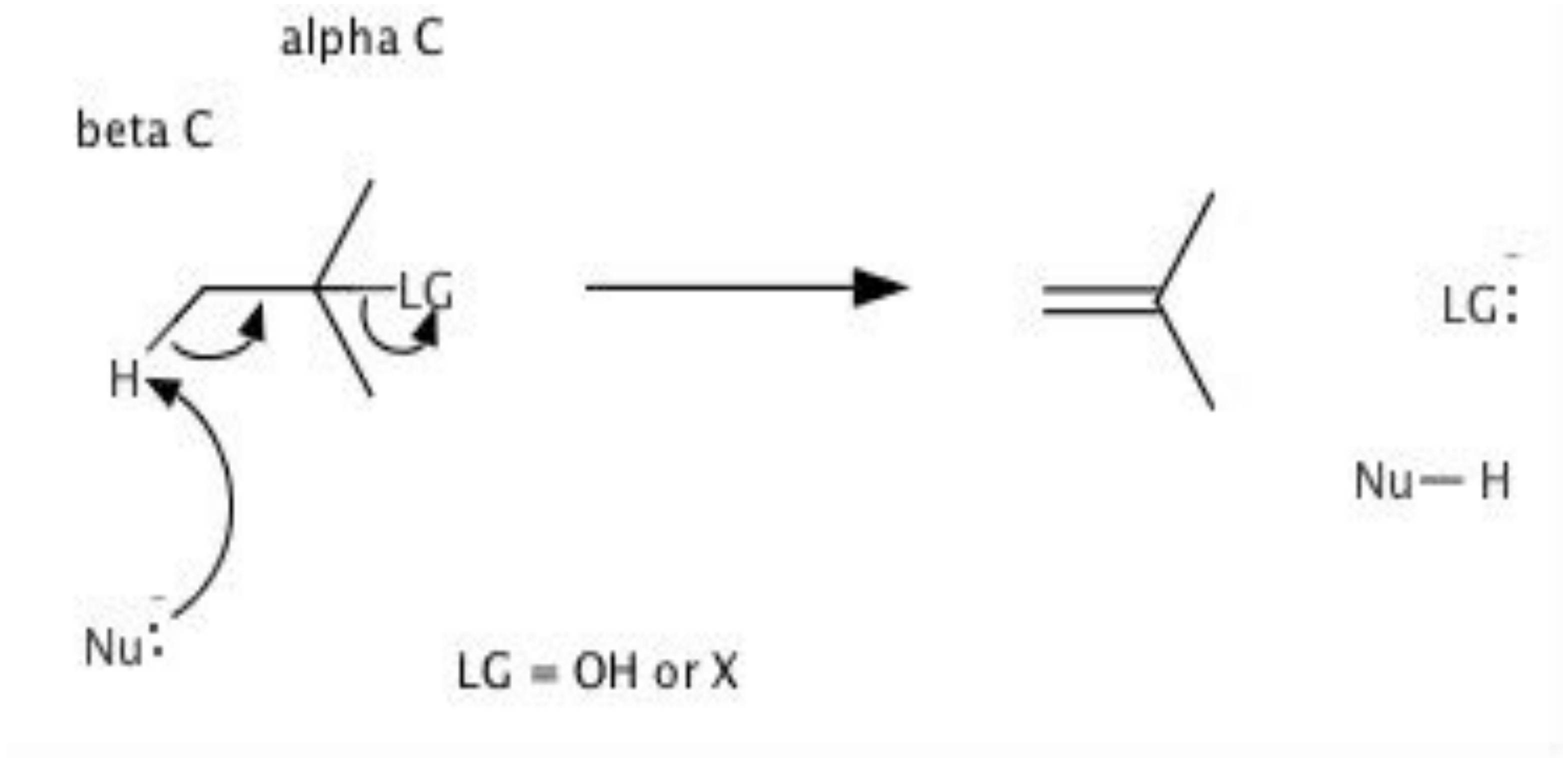
Addition

Substitution

Elimination



Elimination Reaction: Make an Alkene (Synthesis) from RX or ROH

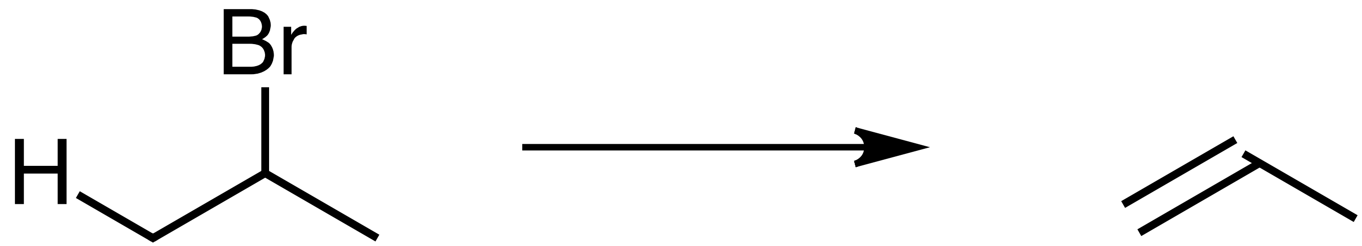


<u>Need</u>: C bonded to Leaving Group (α-C)

Nu:⁻

H bonded to β-C

Elimination Reaction: H on beta C and LG on alpha C are eliminated to form a pi bond.



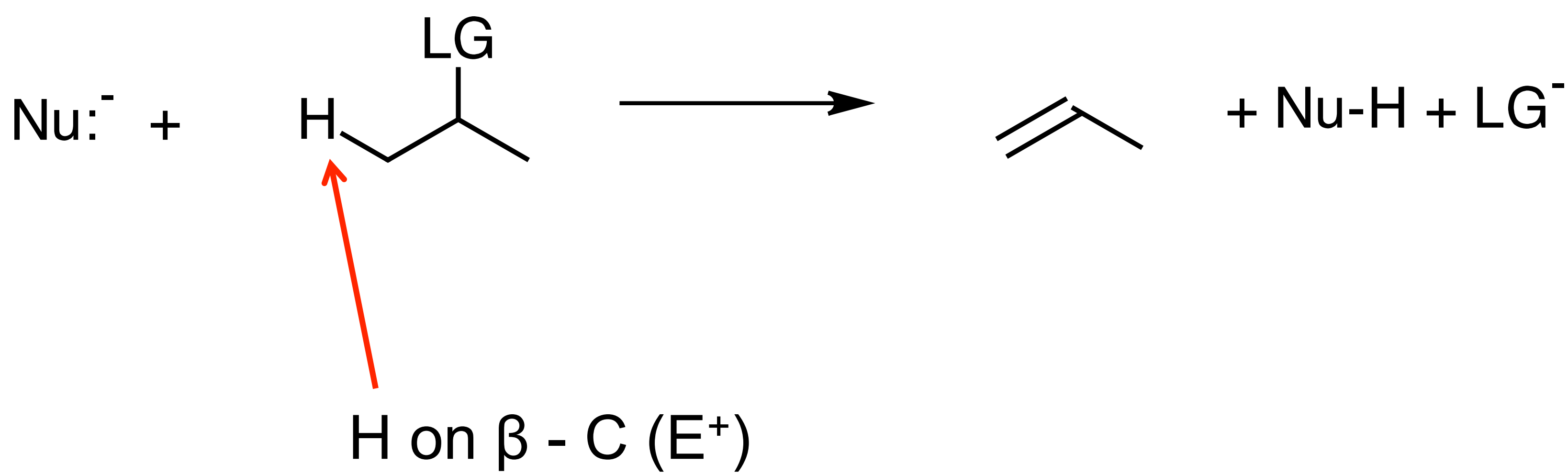
Synthesis: a good way to make a pi bond

Structural Features *for* ***Elimination Reactions***

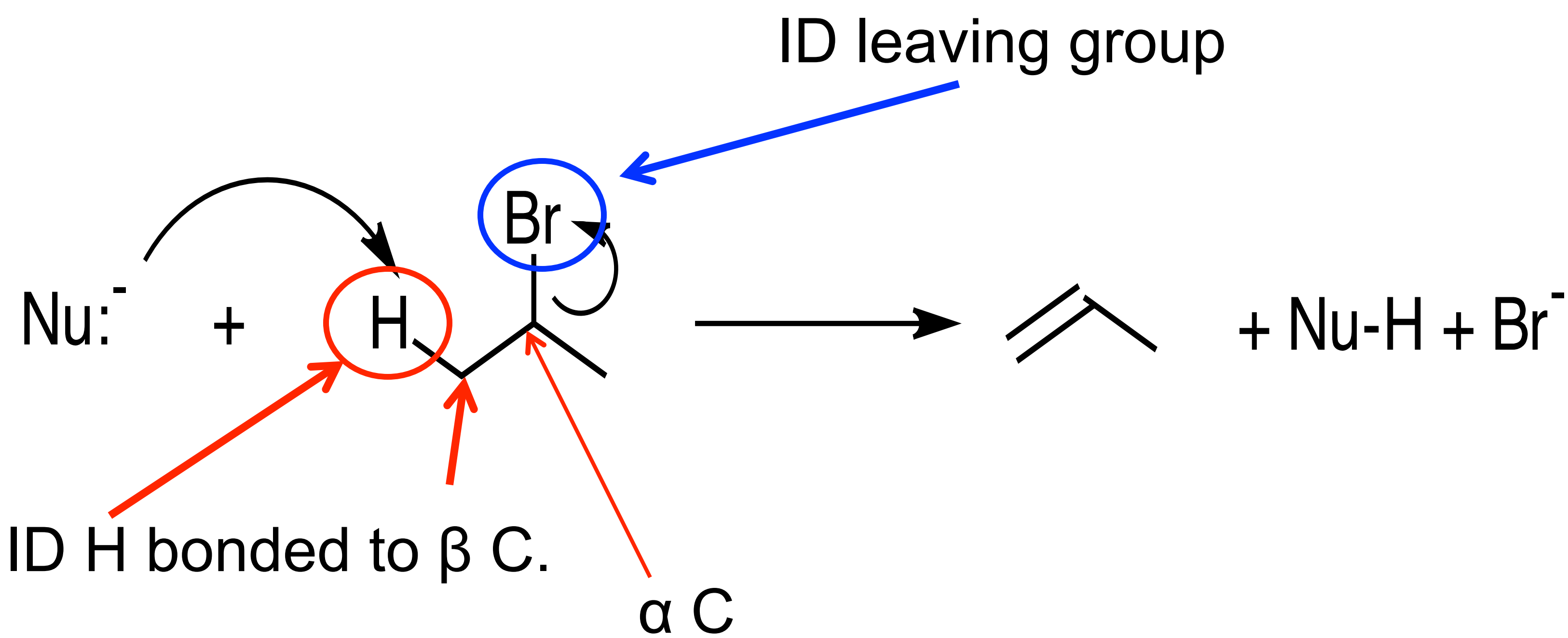
Need a:

1. Nucleophile (Nu:$^-$)
2. Electrophile (E^+) = H on Beta (β) C
3. Leaving Group = a base. See pK_a table.

The **Nucleophile Reacts at H on β C; LG leaves**:

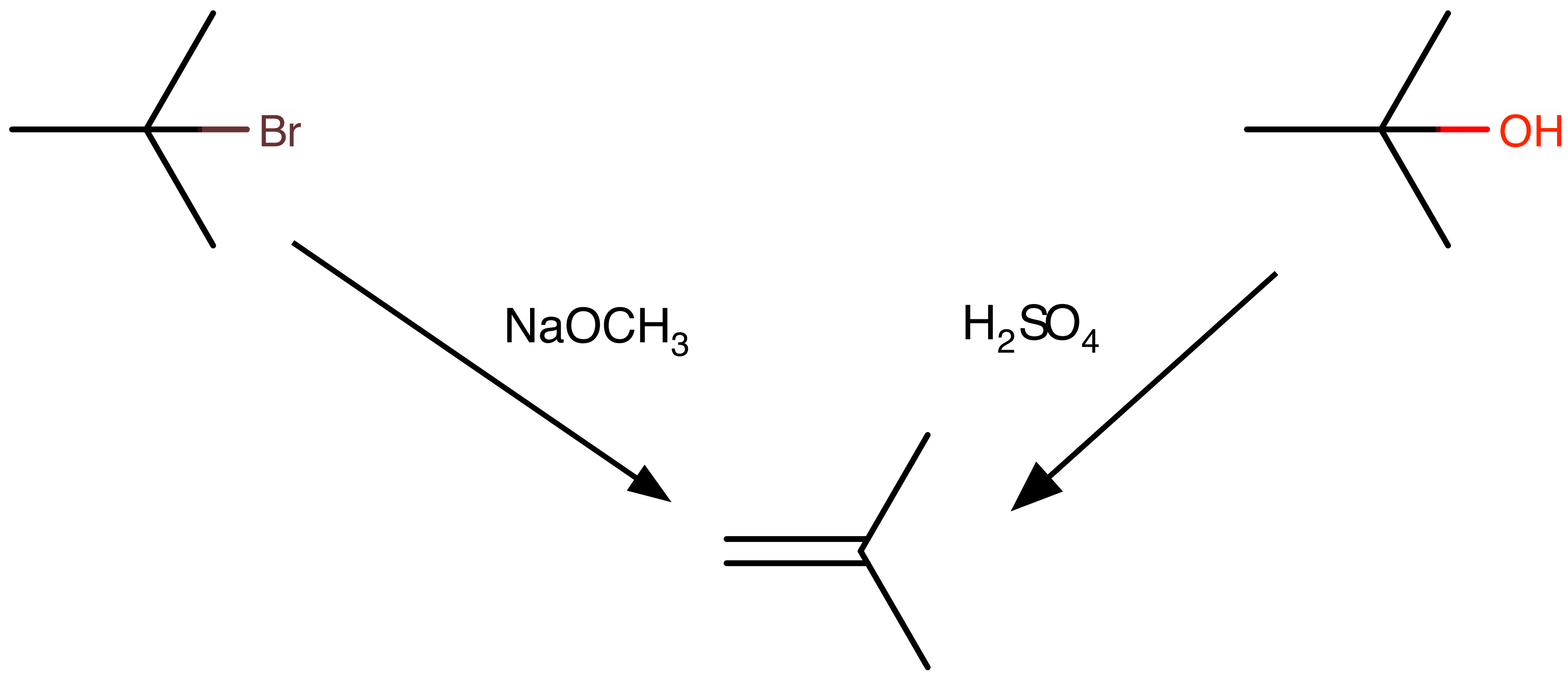


Elimination Reaction: H on beta C and LG on alpha C are eliminated to form a pi bond.



What nucleophile would you use in this reaction?
One curved arrow is missing. Draw this curved arrow to show products form.

Elimination Reaction: Make an Alkene (Synthesis) from RX or ROH

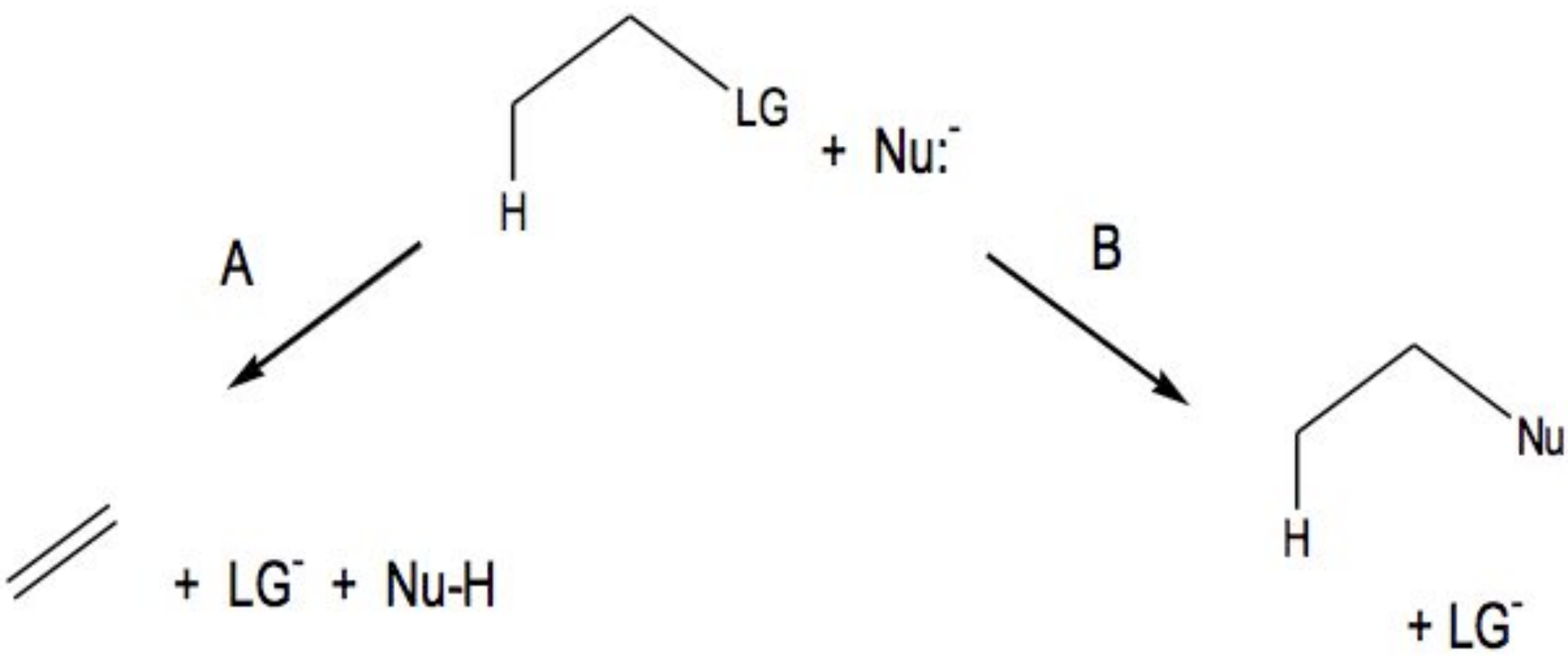


Use curved arrows to show how each reaction occurs.
Why is H_2SO_4 needed in the ROH reaction?

Compare Structural Features of Elimination Reactions to Substitution Reactions:

α-C and LG ➔ Substitution Reaction

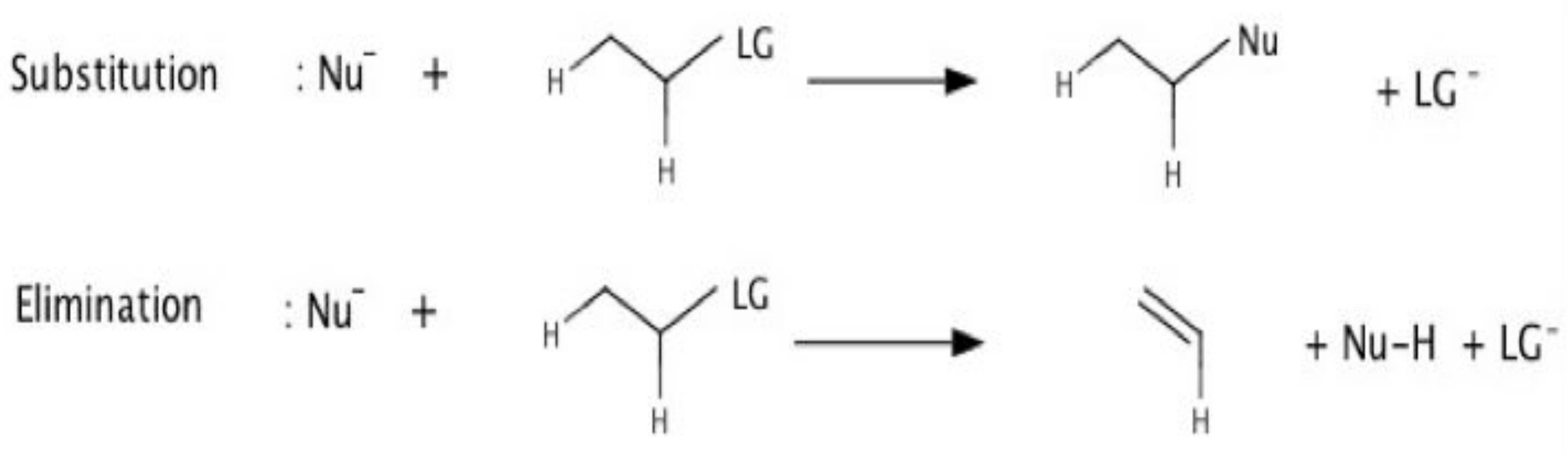
α-C and LG and H bonded to a β-C, ***Elimination*** Reaction



where LG = leaving group and Nu:⁻ = nucleophile

Elimination Reaction:
Make an Alkene (pi bond)

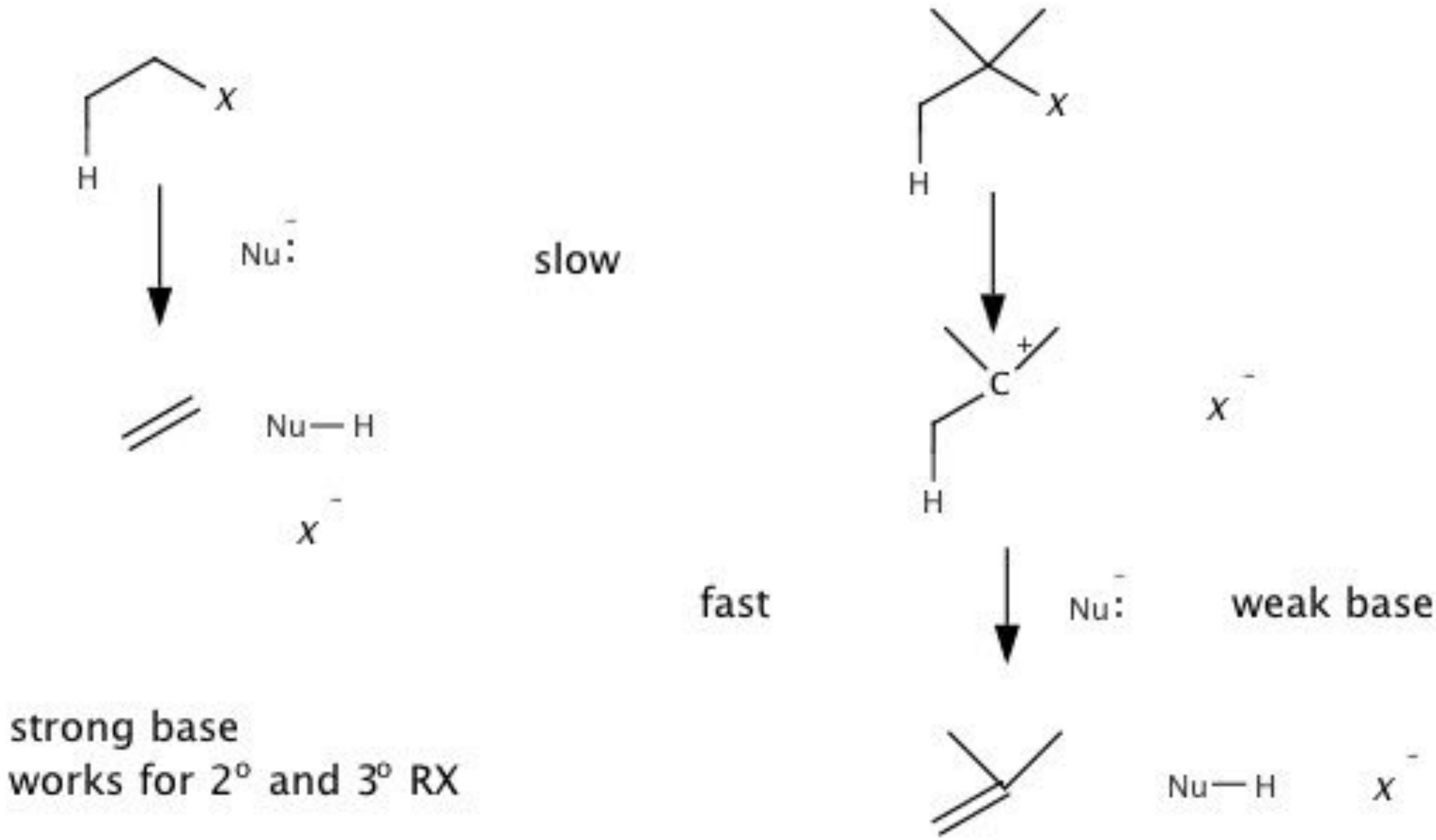
Reactants for an Elimination Reaction are the ***Same*** as a Substitution Reaction



Use curved arrows to show bonds breaking and forming, ID the elemental mechanistic process for each step, and draw a reaction energy diagram.

Two types of Elimination reaction mechanisms to explain RX → alkene and reactivity:

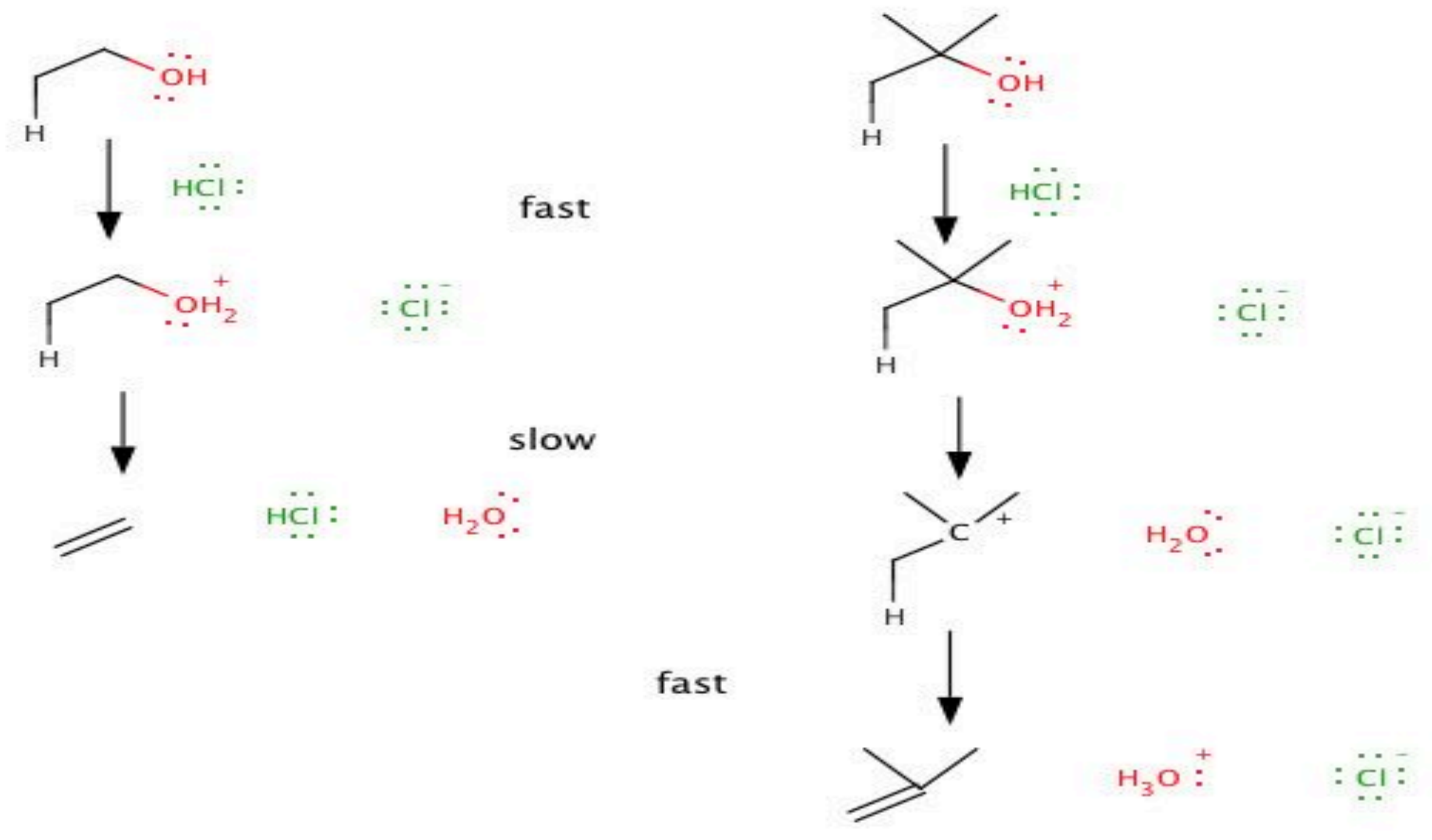
E2 E1



Use curved arrows to show bonds breaking and forming, ID the elemental mechanistic process for each step, and draw a reaction energy diagram.

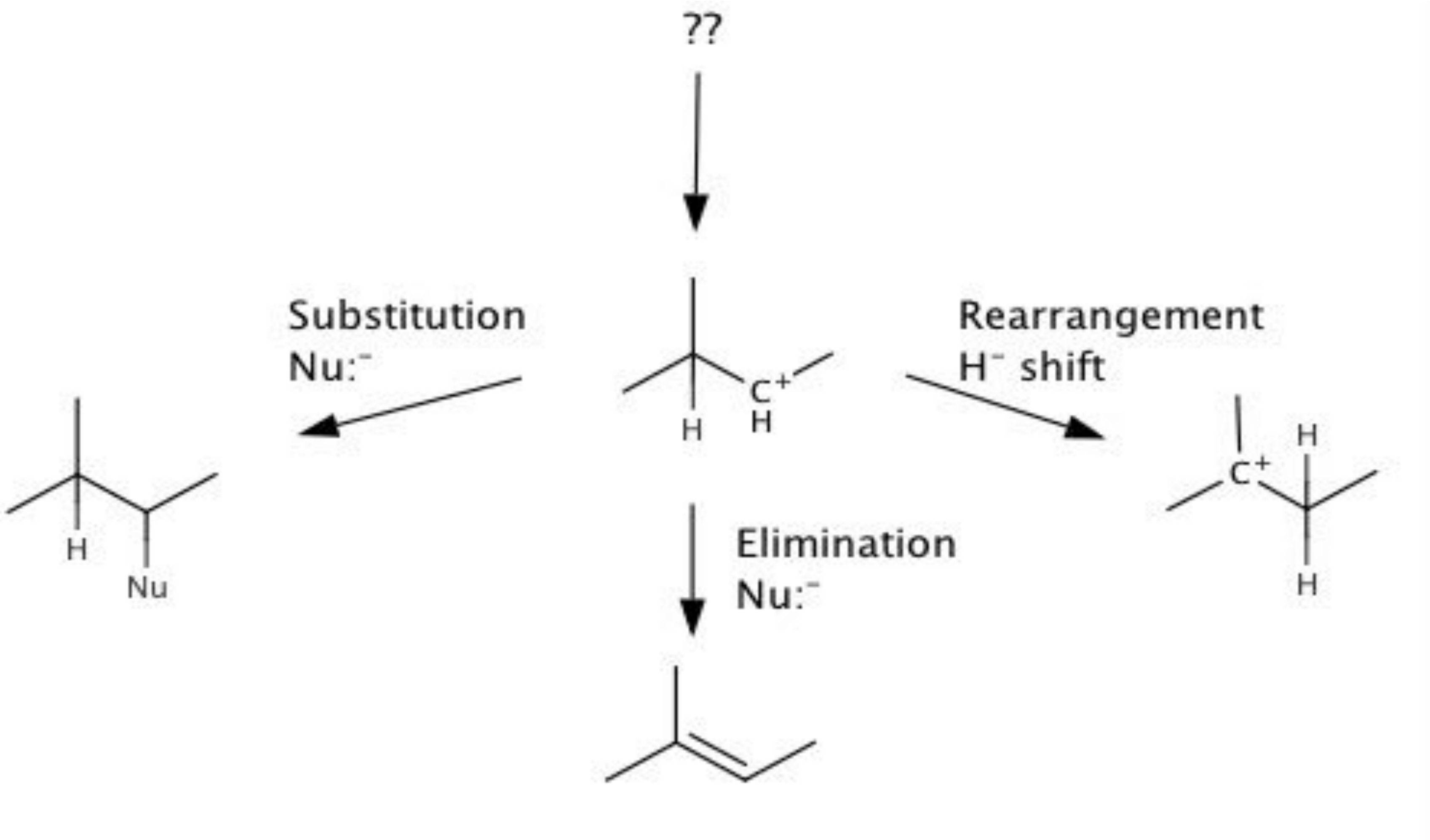
Two types of Elimination reaction mechanisms to explain ROH → alkene and reactivity:

E2 E1



<u>Carbocations</u> (from S_N1 or E1) ***<u>can do 3 things:</u>***

1. React with a (-) charge = Nu:$^-$ (substitution rxn)
2. Eliminate H^+ (elimination rxn)
3. Rearrange to more stable carbocation (H^- or R^- shift)



ROH or RX are Used to Make Alkenes (Elimination Reaction)

Yield of Alkene Product Depends on ***Reaction Conditions***

ROH or RX reactions **that involve a** ***carbocation intermediate may rearrange*****.**

Is this mechanism E1 or E2?

ROH + acid (H_3PO_4, H_2SO_4, $KHSO_4$) --> alkene

RX + weak base (H_2O, C_2H_5OH) --> alkene

RX reactions with a strong base do not rearrange.

Is this mechanism E1 or E2?

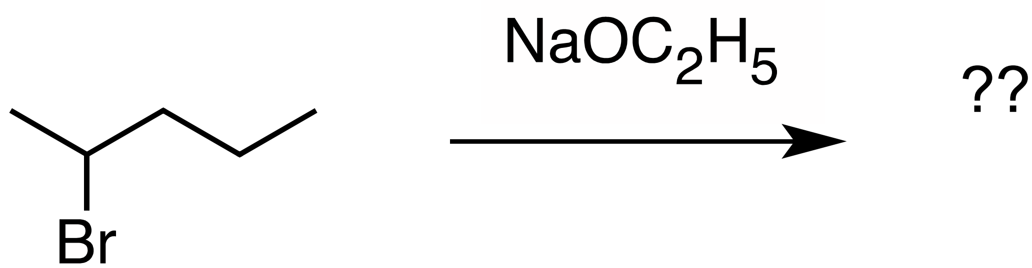
RX + strong base (OH^-, $C_2H_5O^-$) --> alkene

Which reaction conditions give the highest yield?

Objective: Predict the major product

What if a substrate has more than one β-C?

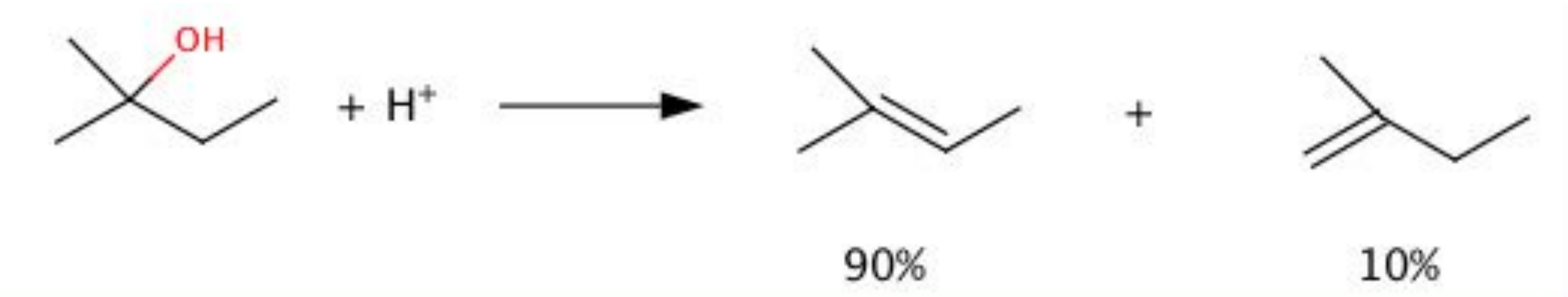
Predict the product of the reaction:



Substrate type? (1°, 2°, 3°)
How many β-C?
What are the possible alkene products?
Which product is more stable?

Zaitsev's rule – *regioselective*

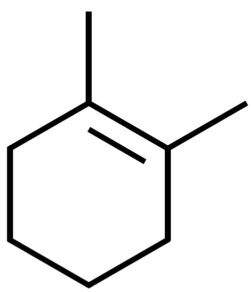
Explain the product distribution:



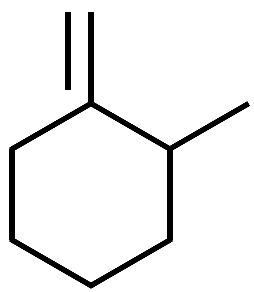
Describe the reaction mechanism. Use curved arrows to show the bond making/breaking processes.

Objective: Make an alkene by an elimination reaction.

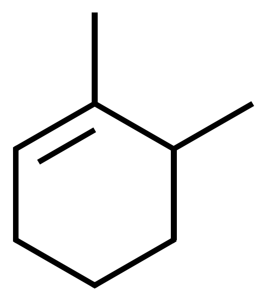
Describe a synthesis of each compound.
Which reactant would you use?



A



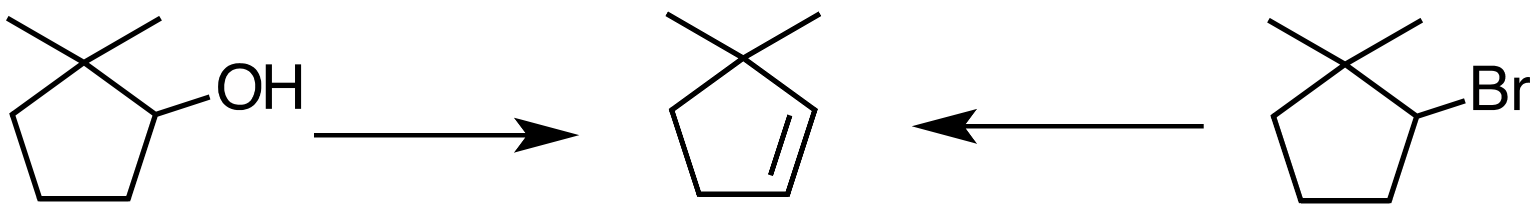
B



C

You have available 2,2-dimethylcyclopentanol (A) and 2-bromo-1,1-dimethylcyclopentane (B) and wish to prepare 3,3-dimethylcyclopentene (C). Which would you choose as the more suitable reactant, A or B, and with what would you treat it?

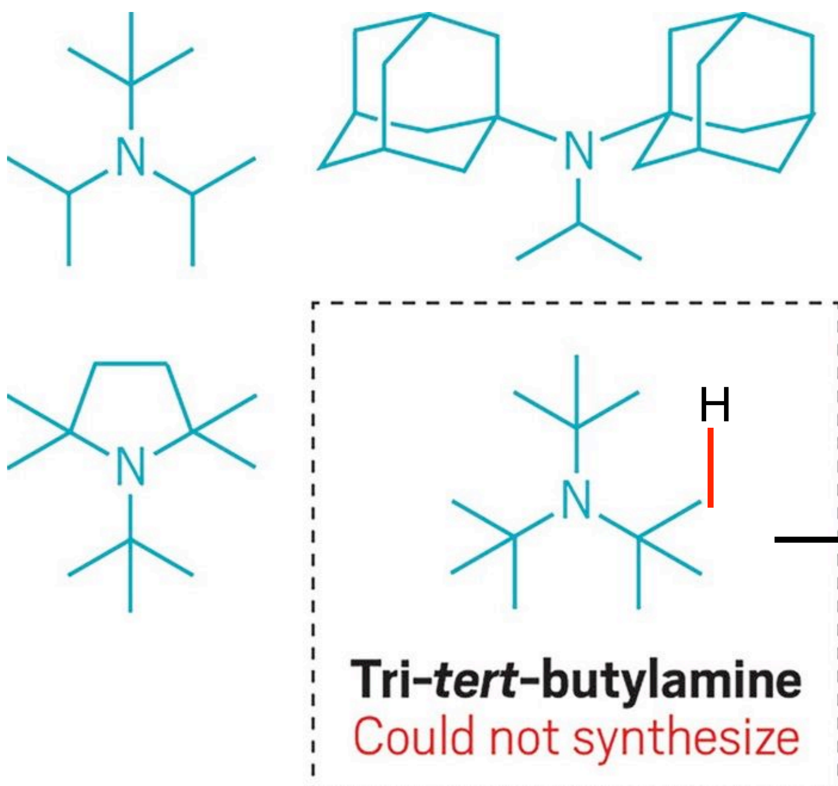
See Practice Problem 6d.

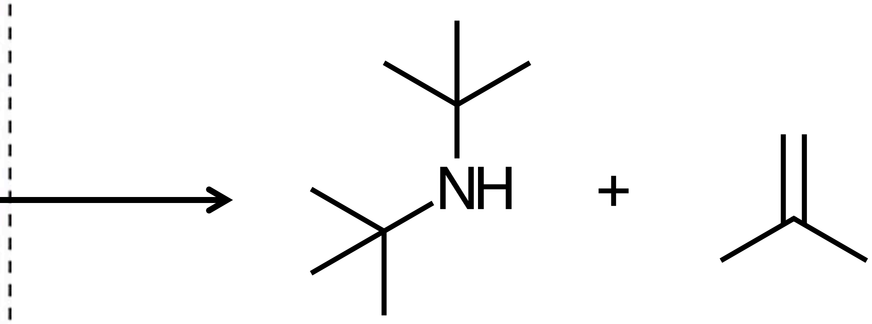


A C B

"*Bulking up trisubstituted amines*" (CEN, 5/7/18, p. 9)

Bulky, trisubstituted amines are hard to make because they tend to undergo elimination reactions.





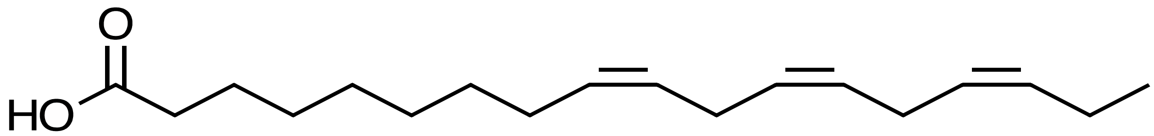
Use curved arrows to show how the products form.

Many alkenes are found in nature.
E.g., unsaturated fats and oils

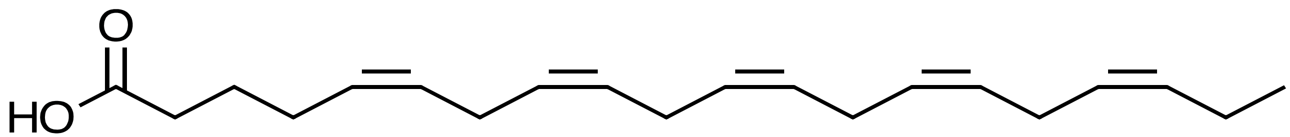
Synthesis:
Industry - Alkenes are important starting materials to make different compounds.
E.g., ethylene and propylene are in the Top 20 chemical produced in the US. Each are used to make plastics, solvents, fibers.

Make an alkene by an elimination reaction.

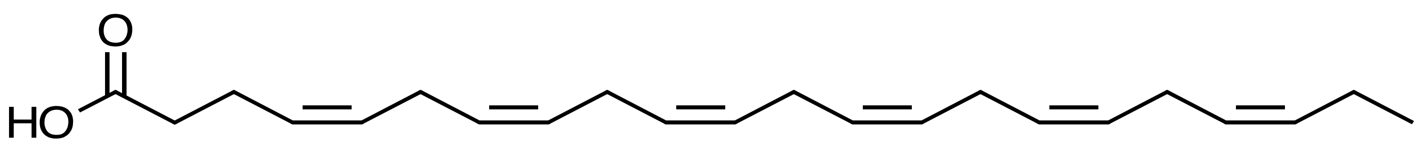
Unsaturated Fats contain a C=C bond(s)



alpha-linolenic acid (ALA) - flax seed



eicosapentaenoic acid (EPA) - fish oil

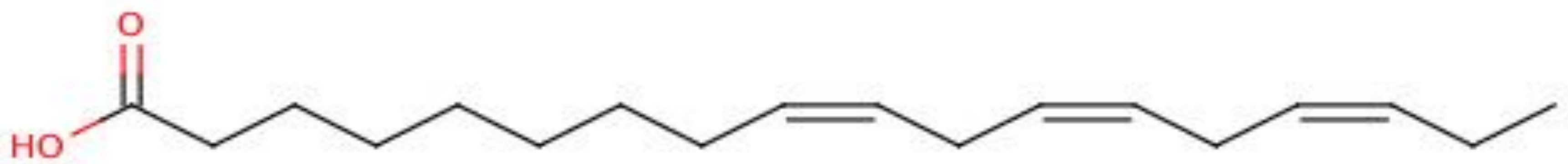


docosahexaenoic acid (DHA) - fish oil

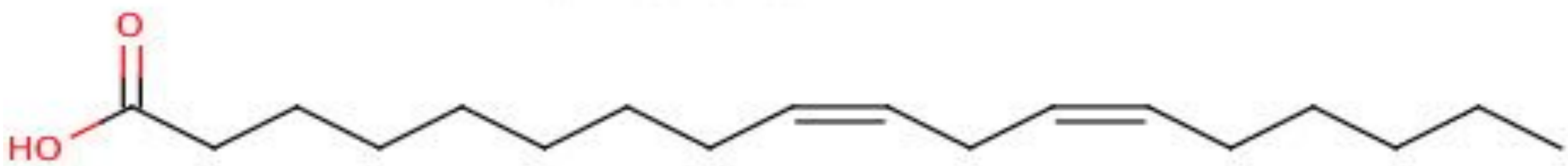
Essential fatty acids (EFA) are Omega-3 fatty acids and Omega-6 fatty acids. E.g., DHA is involved in neural development.

These acids differ in the **location** of the C=C double bond.

Which fatty acid below is an omega-3 fatty acid?



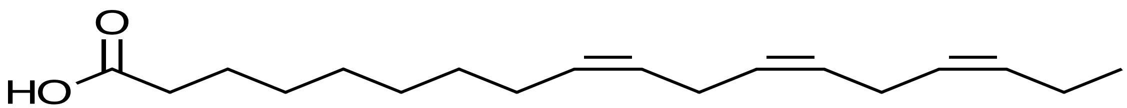
a-linolenic acid



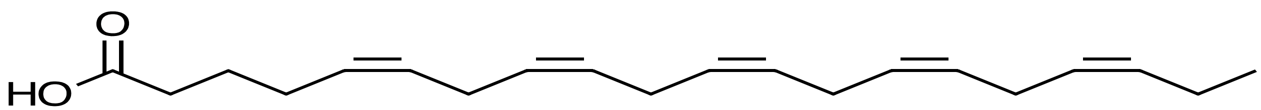
linoleic acid

Omega-3 fatty acids: C=C starting on 3rd C from end, cis

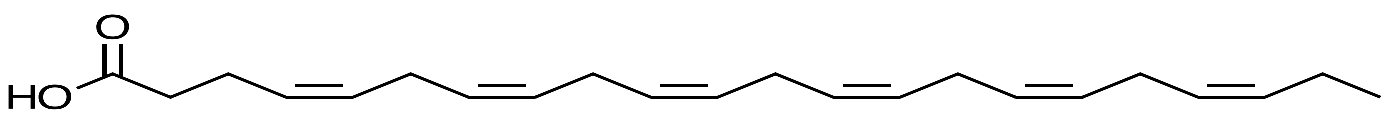
alpha-linolenic acid (18:3, n-3; ALA) EFA
eicosapentaenoic acid (20:5, n-3; EPA) EFA
docosahexaenoic acid (22:6, n-3; DHA) EFA



alpha-linolenic acid (ALA) - flax seed



eicosapentaenoic acid (EPA) - fish oil



docosahexaenoic acid (DHA) - fish oil

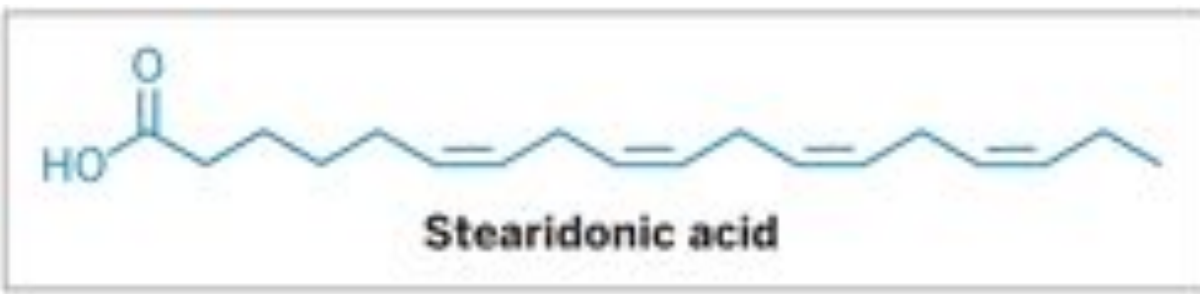
Omega-6 fatty acids: final C=C on 6th C from end, cis

Linoleic acid (18:2, n-6) EFA
Arachidonic acid (20:4, n-6) precursor to prostaglandin

Fish don't make omega-3 fatty acids; ***omega-3 fatty acids come from the algae the fish consume.*** (CEN, 8/11/08, p. 39)

Scientists have begun to transplant into plants the genes that allow algae to synthesize omega-3 fatty acids. Oceans can't support our current level of fish consumption, so land-based plants may be more sustainable sources of these valuable fatty acids.

Monsanto genetically engineered a soybean plant enriched in stearidonic acid (SDA).

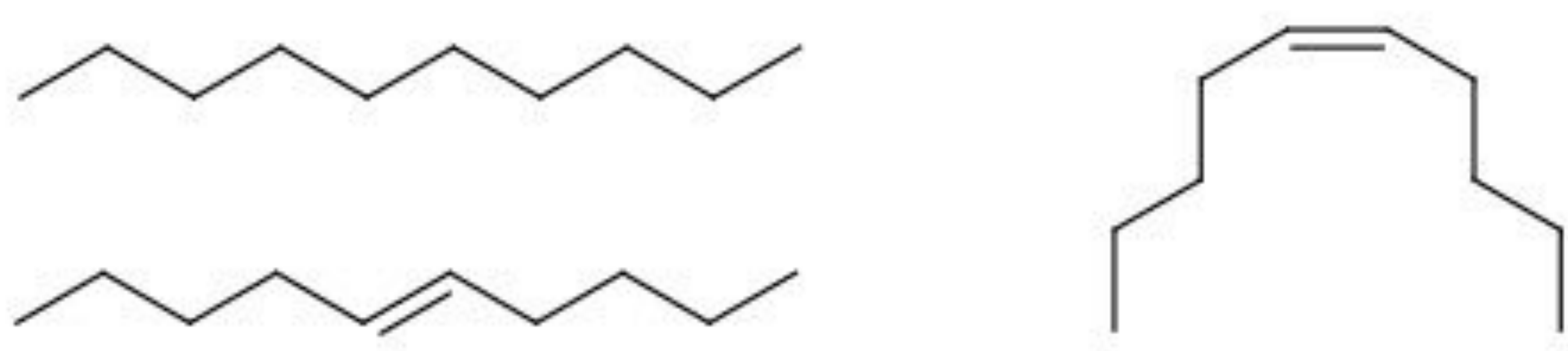


SDA is a short-chain omega-3 fatty acid, one humans can use as a precursor to make longer chain omega-3 fatty acids such as EPA and DHA.

"It Is Better To Eat Bent Molecules Than Straight Molecules"

http://scifun.chem.wisc.edu/chemweek/pdf/Fats&Oils.pdf
http://www.journeytoforever.org/biofuel_library/fatsoils/fatsoils1.html
http://recipes.howstuffworks.com/fat.htm
http://biology.clc.uc.edu/Courses/bio104/lipids.htm

Which molecule is saturated? Unsaturated? Cis? Trans?

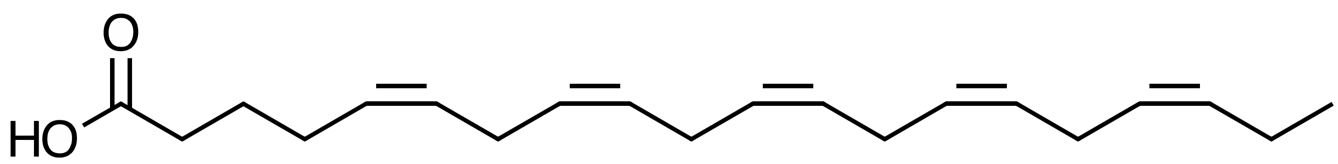


Straight Molecules - Saturated Fats and Trans Unsaturated Fats
Bent Molecules - Cis Unsaturated Fats

Simplest Fats Are Fatty Acids - hydrocarbon chain with acid group

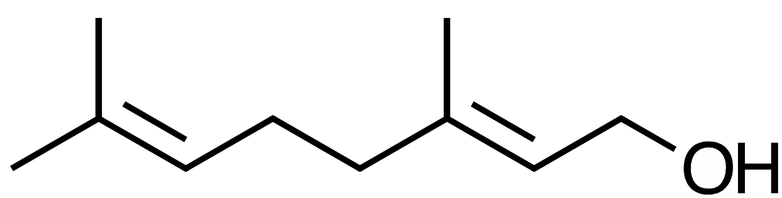
Objective: Identify cis/trans or E/Z isomer

Is EPA cis or trans?



eicosapentaenoic acid (EPA) - fish oil

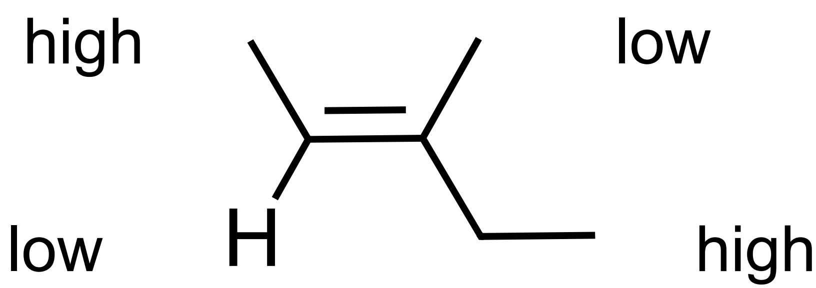
Geraniol (essential oil from roses) has two C=C bonds. Is the C_2-C_3 configuration E or Z?



Objective: Identify cis/trans or E/Z isomer

Di-, tri-, and tetrasubstituted alkenes have *isomers*:
Disubstituted on adjacent C’s: cis/trans (stability: trans > cis)

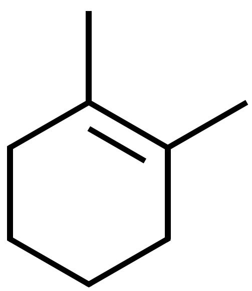
Tri- and Tetrasubstituted: E/Z
Priority rules for E/Z are based on atomic weight (*just like R/S*).



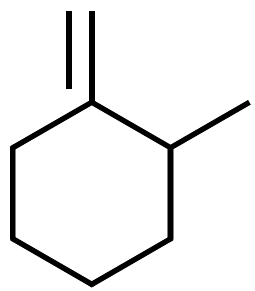
(2E)-3-methyl-2-pentene

Objective: Identify the most stable alkene

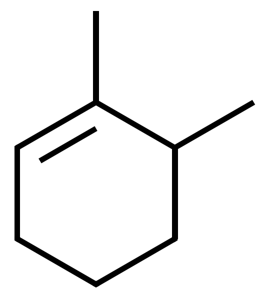
Which compound is the most stable?



A



B

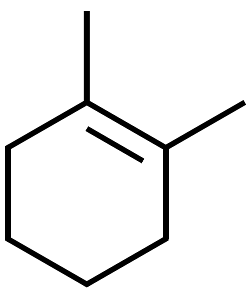


C

Objective: Identify the most stable alkene

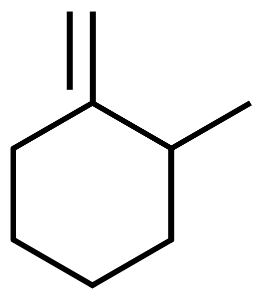
TetraSubstituted Alkenes are the **Most Stable**

Tetra- > Tri- > Di- > Mono-



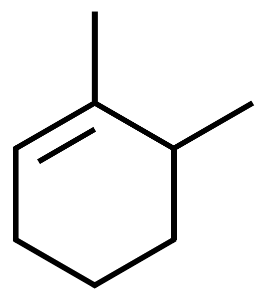
A

Tetrasub
Most
stable



B

Disub
Least
stable



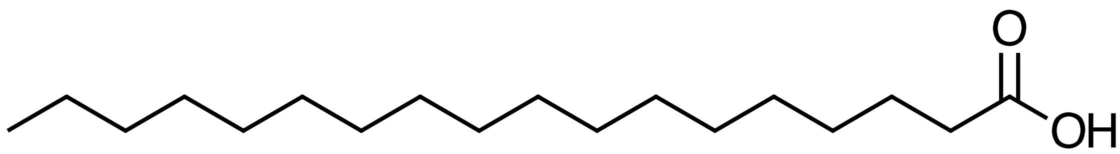
C

Trisub

Fats are Solids; Oils are Liquids

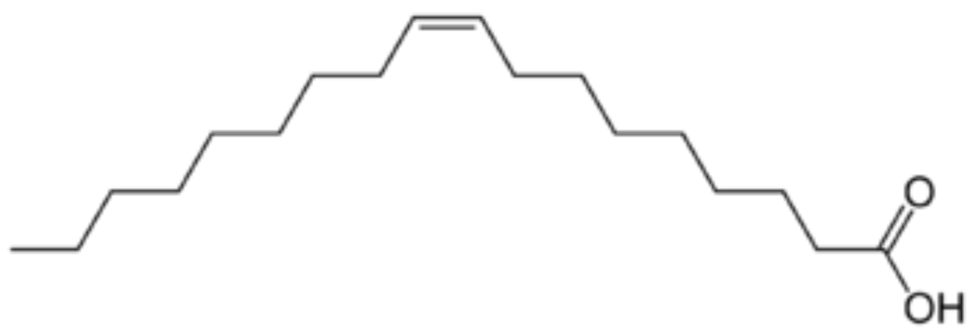
Based on melting point, why are unsaturated fats better for you than saturated fats?

Straight molecules pack closer together than bent molecules.



Stearic acid
m.p. = 69°C

Oleic acid
m.p. = 14°C



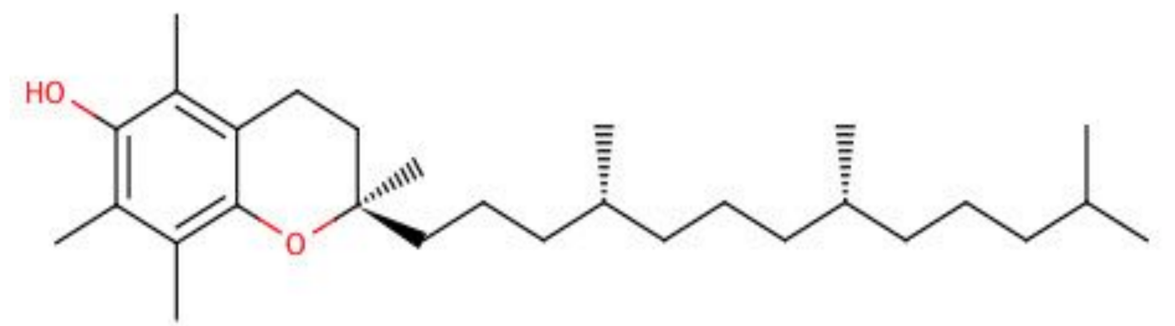
Based on stability, is it better to eat <u>bent</u> molecules or <u>straight</u> molecules?

trans is more stable than cis (see Carey, 8th ed., Fig. 6.1, heat of hydrogenation energies, p. 229) - why?

Based on bonding, are unsaturated fats better for you than saturated fats?

Vitamin E (antioxidant) is added to unsat'd fats to prevent rancidity.

α-tocopherol form of Vitamin E found in wheat germ, sunflower, safflower oils. Antioxidant stops production of reactive oxygen species formed when fat undergoes oxidtion.
http://en.wikipedia.org/wiki/Vitamin_E



Unsaturated Fats, especially polyunsaturated fats, go rancid

Three pathways:

Hydrolytic - ester hydrolysis (Chem 12B) of trigylcerides

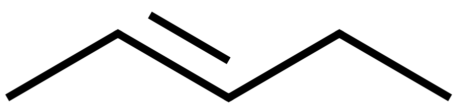
Oxidative - the double bonds of an unsaturated fatty acid can undergo cleavage, releasing volatile aldehydes and ketones (Ch. 9)

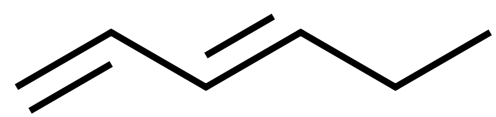
Microbial (http://en.wikipedia.org/wiki/Rancidification)

Objective: Naming alkenes

The π bond in an Alkene is labeled by the C #.
Which C is the vinyl carbon?
Which C is the allylic carbon?

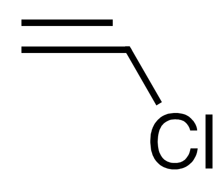
Name each compound.





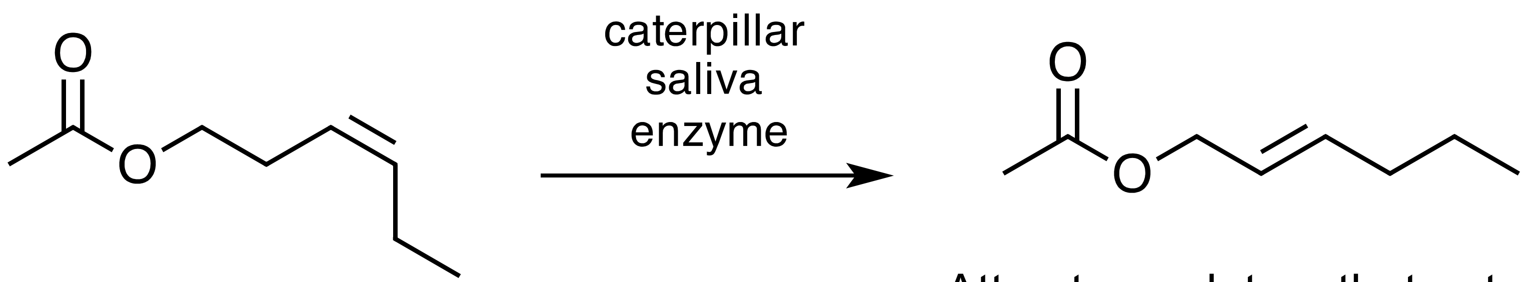
Is each C=C bond the same length?

Vinyl chloride - Precursor to plastic (PVC)



http://cen.acs.org/articles/91/i23/Isomerizing-Saliva-Guides-Moth-Egg.html

6/10/13, CEN, p. 28 Hawk moths sniff out the best place to lay eggs by avoiding leaves on which caterpillar saliva enzymes produce a predator-attracting odor



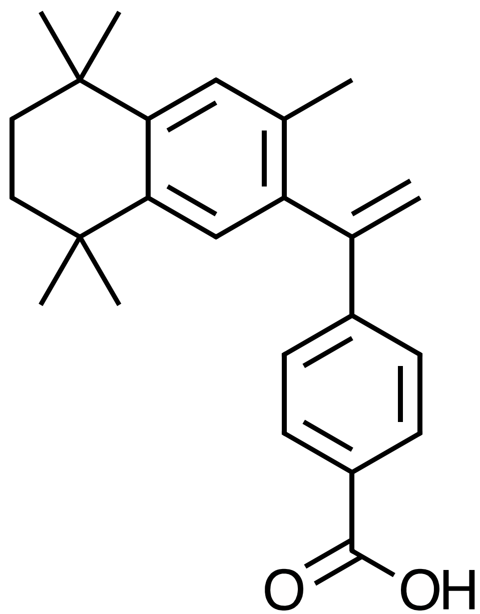
Attracts predators that eat caterpillars and their eggs; but repels hawk moths from laying eggs on leaves that caterpillars can eat

Name each acetate compound.
Include cis/trans or E/Z in name.
___-__-______ acetate

http://cen.acs.org/articles/91/i23/Alzheimers-Treatment-Dispute.html

6/10/13, CEN, p. 30 Bexarotene possible Alzheimer's Treatment

2012 study indicated bexarotene reversed neurodegeneration in mice but results can't be replicated

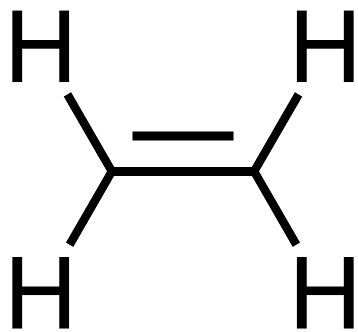


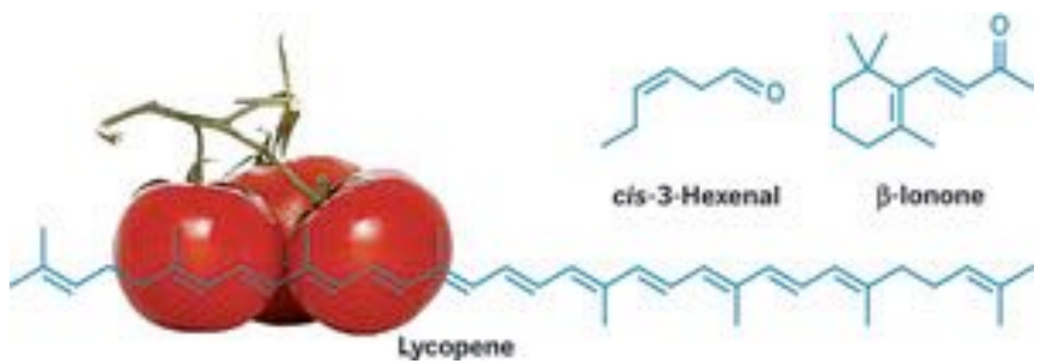
Bexarotene: cis or trans or E or Z?

Ethylene is a plant ripening hormone (CEN, 10/29/07, p. 10)

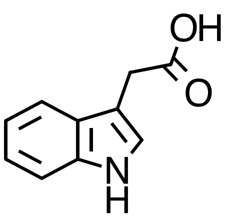
Gene → (ripening hormone) → enzyme →

- Plant pigment
- Aromatic volatiles
- Convert starch to sugar
- Break down cellulose and pectin (soften)

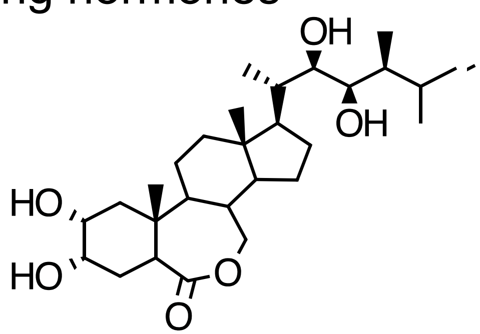




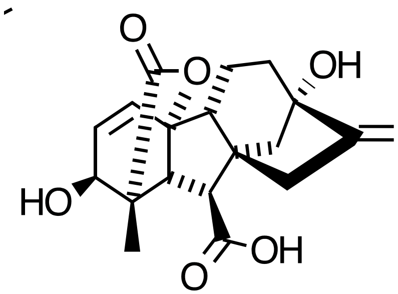
Other ripening hormones



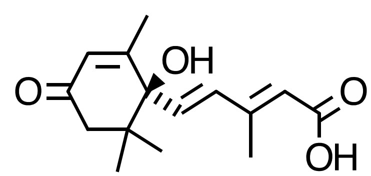
Auxin



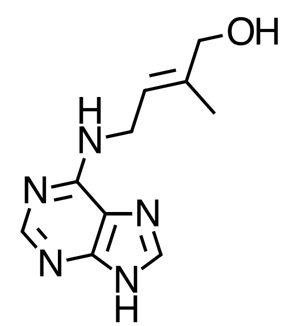
Brassinolide



Gibberellic acid



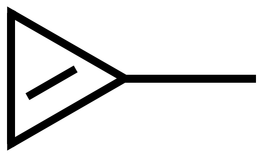
Abscisic acid



Cytokinin

2006: *65 million tons* of fresh fruits and vegetables exported

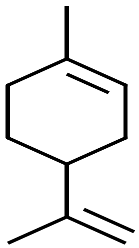
Single ripening banana can spur the ripening of an entire banana shipment. $KMnO_4$ is used to absorb or inactivate C_2H_4.



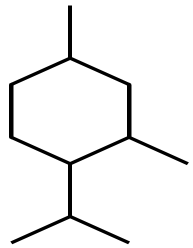
1-methylcyclopropene inhibits ripening

Fruit ripeness sticker (CEN, 8/`4/06, P. 72): Mark Riley (U. of Arizona) has developed a RediRipe sticker that can indicate when a fruit or vegetable has reached optimal ripeness. Increasing levels of ethylene cause the sticker to change from white to increasingly deeper shades of blue over a period of 24 to 48 hours. (The sticker cannot detect overripe or rotten fruit, and not all produce emits enough ethylene for the sticker to detect.)

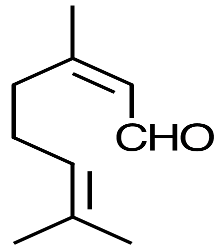
Terpenes are found in Natural Products and contains 5x carbons (isoprene unit)



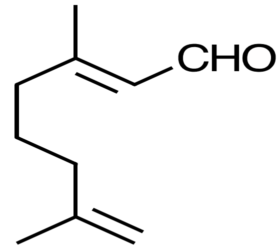
Limonene
citrus



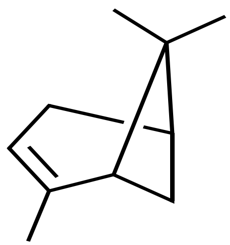
Menthol
(mint)



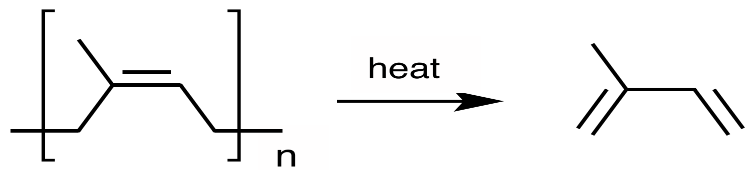
Citronellal
(citronella)



Citral
(lemongrass)

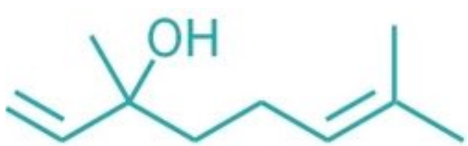


Pinene
(pine turpentine)



Natural Rubber

Isoprene



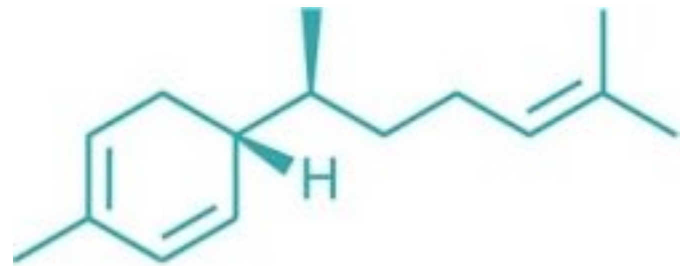
Linalool

Lavendar oil (antiseptic and antioxidant)

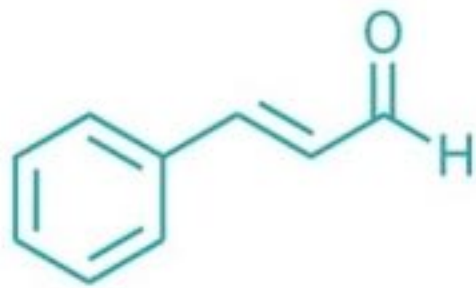
http://cen.acs.org/articles/92/i41/Problem-Lavender-Oil.html

Pumpkin Spice –Flavor of the Month
Contains Terpenes

http://cen.acs.org/articles/92/i43/Pumpkin-Spice-Flavor.html



Zingiberene

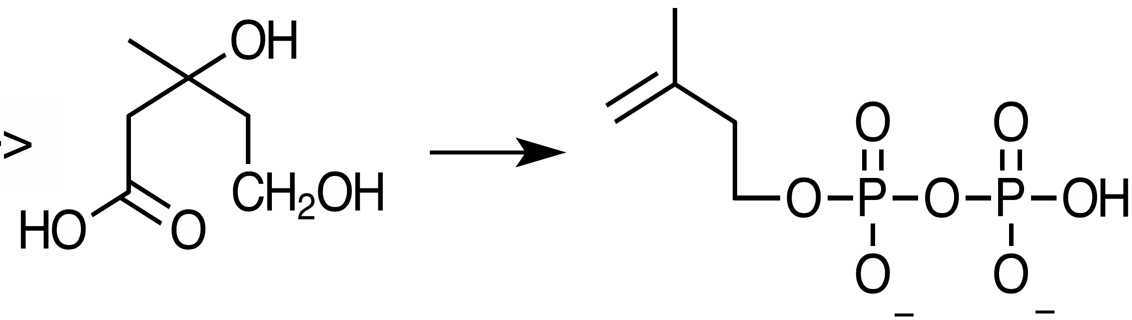


(*E*)-Cinnamaldehyde

Sabinene

Terpenes are made from Mevalonic Acid:

Glucose ---> Acetyl Co-A --->



Mevalonic Acid

Isopentyl pyrophosphate