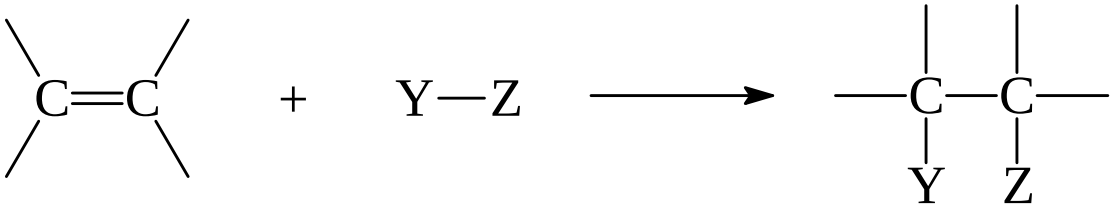
Reactions of Alkenes

Typical type: addition



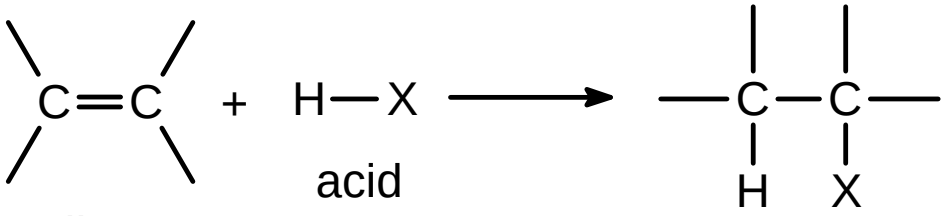
substrate reagent product

Mechanism: Usually not one simple step.

Weaker π-bond broken, also Y - Z bond. Energy provided by formation of C - Y and C - Z bonds.

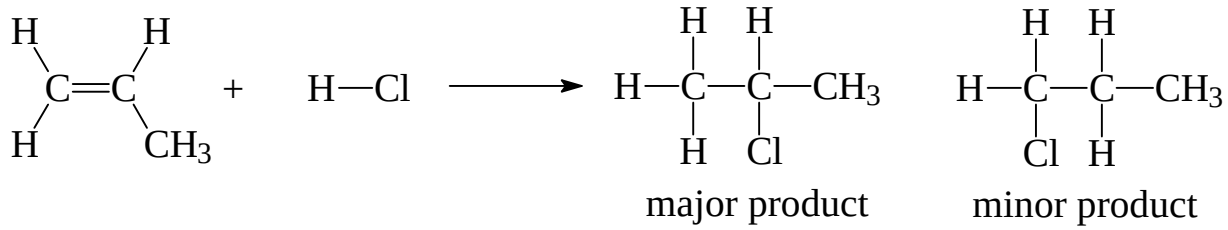
π-bond: source of electrons.
Reagent: typically electrophile or free radical.
Therefore, electrophilic or free radical addition.

Addition of Acids & Markovnikov's Rule



alkene acid alkyl halide

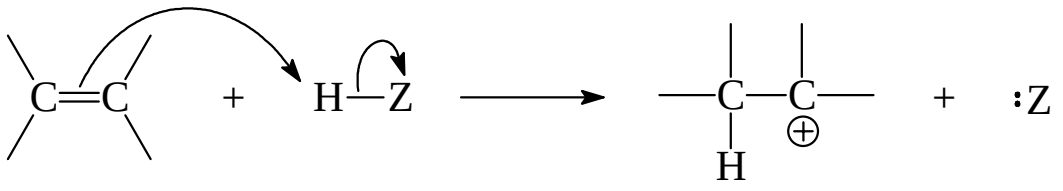
HX = HCl, HBr, HI (or KI + H_3PO_4), HOH (with H_3O^+)



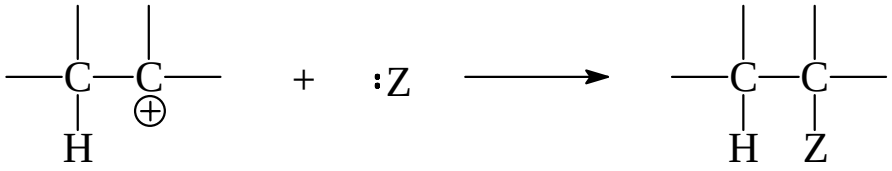
Markovnikov rule: Polar (ionic) addition of an acid to a double bond --- the hydrogen preferentially attaches itself to the carbon which already has the greater number of hydrogens directly attached. This preference is strong. HCl, HBr, HI (or KI + H_3PO_4) and H_2O follow this rule.

However, in the presence of peroxides,
R - O - O - R', HBr (only) will add the opposite way: anti-Markovnikov

These are highly *regioselective* or *regiospecific* reactions.

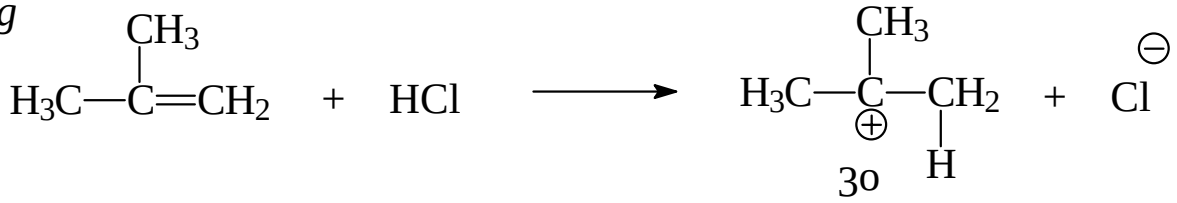
(1) 

HZ = HCl, HBr, HI, H_3O^+

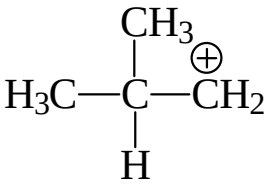
(2) 

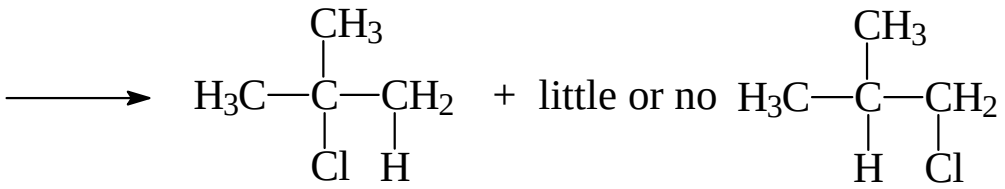
Step 1 is rate limiting.

eg

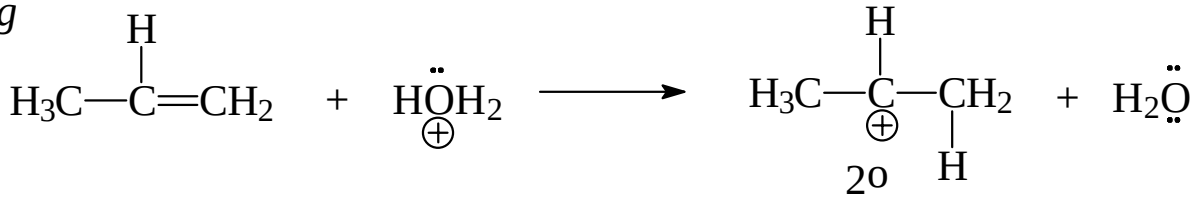


3o

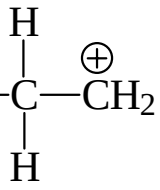
3o carbocation is formed faster than 1o: 

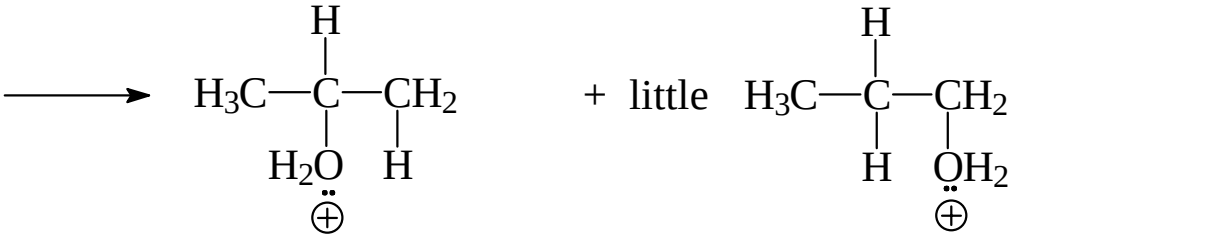


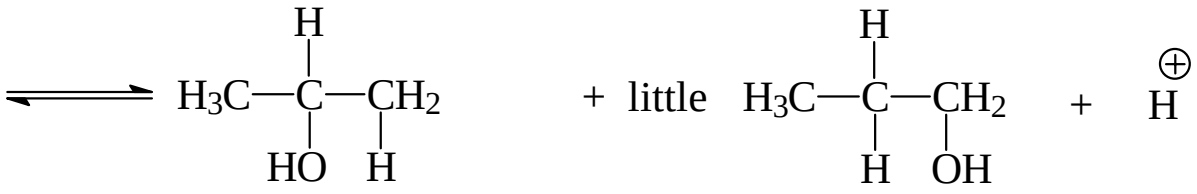
eg



2o

2o carbocation is formed faster than 1o: 





(Fun) fact #1 about carbocations:

The order of stability of carbocations is:

3^o (tertiary) > 2^o (secondary) > 1^o (primary) > methyl
most stable least stable

Reason: Charge and electrons are most *delocalized* in 3^o and most *localized* in methyl. [It can be shown by quantum mechanics that spreading electrons over a larger volume of space --- delocalization --- leads to lower energy.]

The electrons are more delocalized in the more highly substituted carbocations because of

- ☞ an inductive effect: alkyl groups are larger and more polarizable than hydrogen atoms, and
- ☞ a hyperconjugation effect.

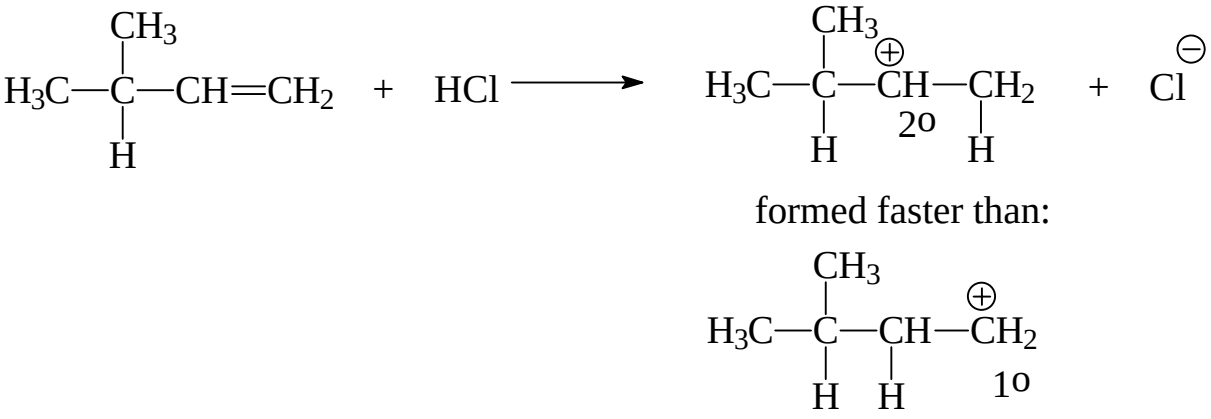
Thus, orientation of addition (regioselectivity) seems to depend on the formation of the more stable carbocation; in other words the more stable carbocation is formed (much) faster.

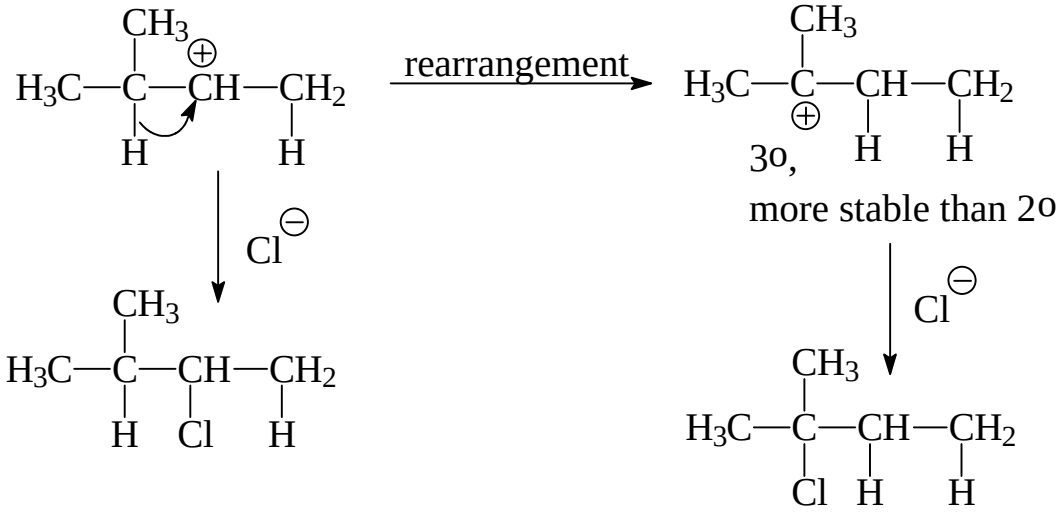
Why?

It is also usually true that the relative reactivity of two different alkenes will depend on which forms the more stable carbocation.

(Not so fun) fact #2 about carbocations:

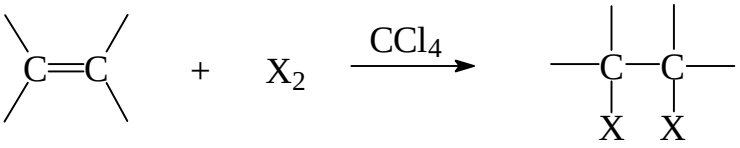
They rearrange, *eg*





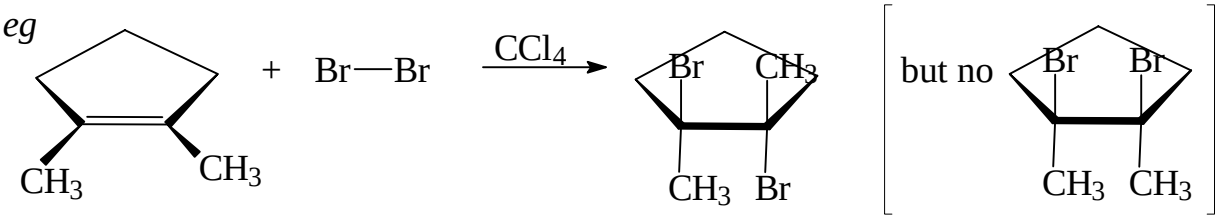
Electrophilic Addition with Electrophiles Other Than H^+

Halogenation ---



$X_2 = Br_2$ or Cl_2

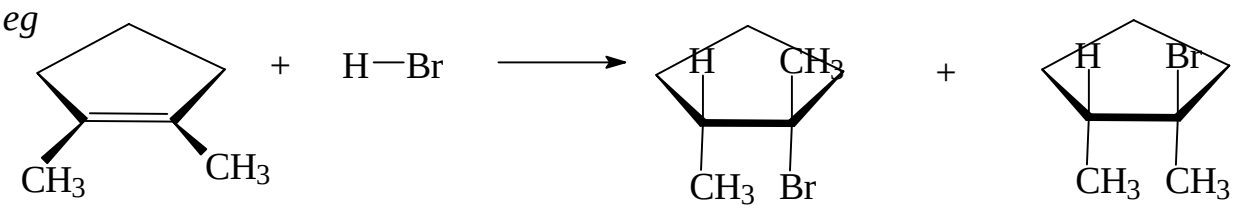
eg



ANTI ADDITION ONLY

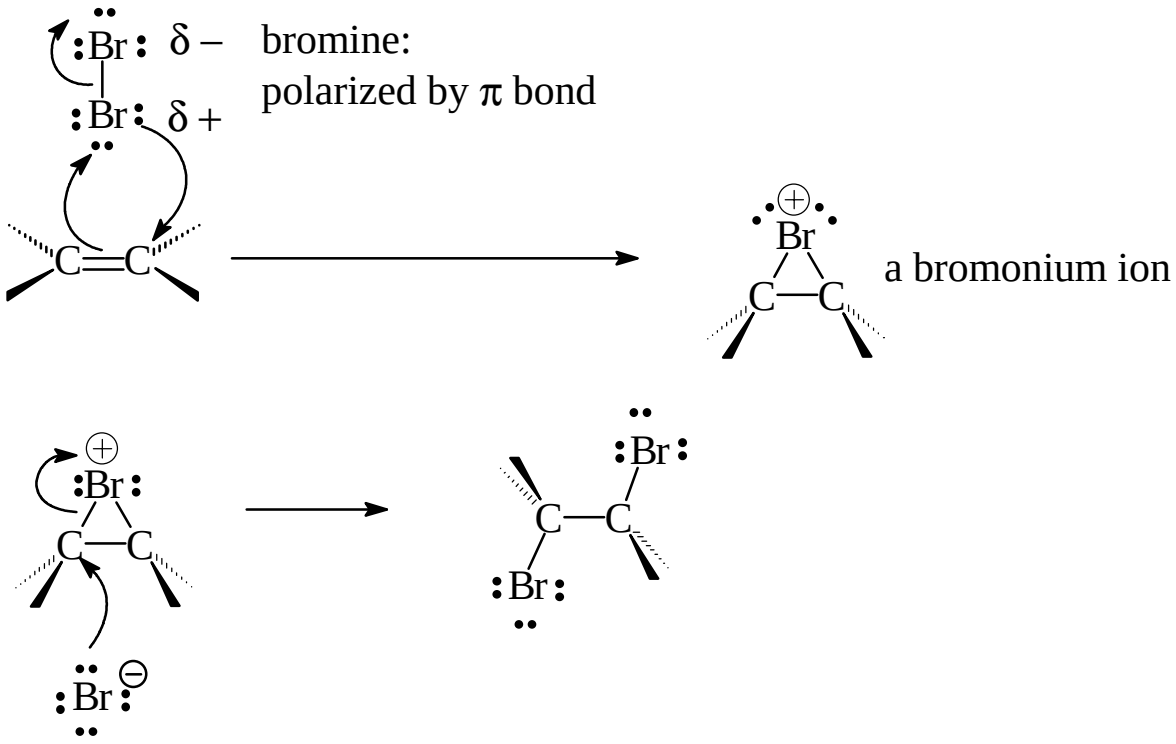
This may be contrasted with the addition of HX to an alkene where syn and anti addition are observed ---

eg



ANTI AND SYN ADDITION

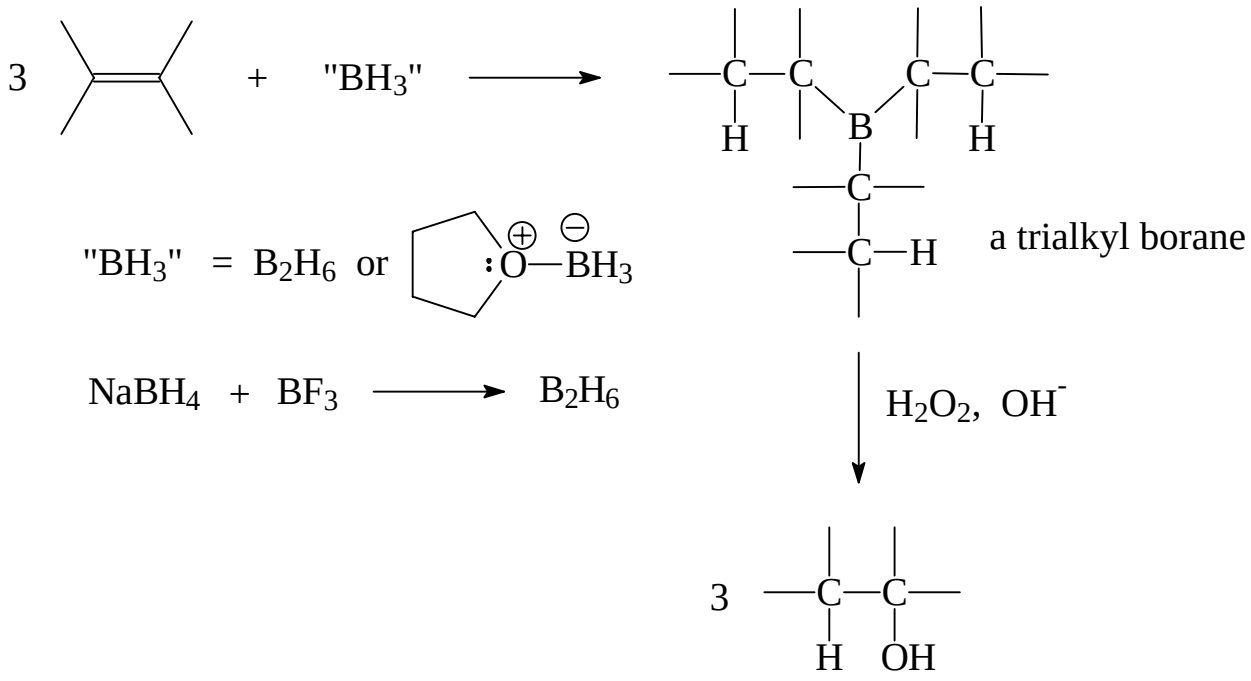
Mechanism —



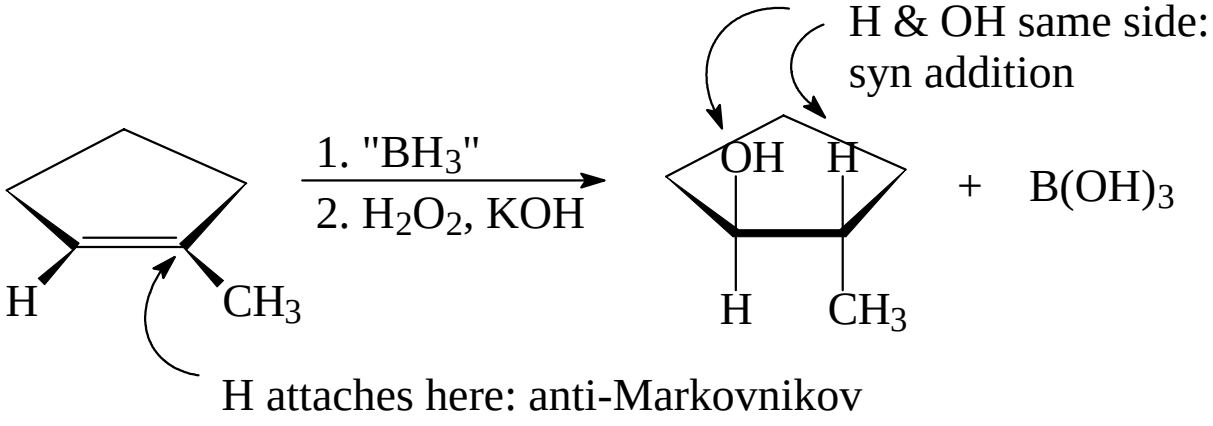
A proton, unlike bromine, is not large enough to form a 3-membered ring intermediate; it forms an open carbocation.

Alcohols *via* Hydroboration - Oxidation ---

Anti-Markovnikov, syn addition of H and OH to a double bond to form an alcohol.



An example ---

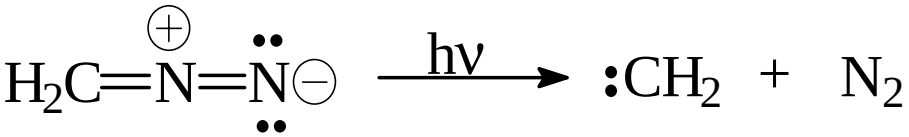


Addition of Carbenes to Alkenes: Cyclopropane Synthesis ---

A *carbene* is a neutral molecule containing a divalent carbon with 6 electrons in its valence shell ---

R_2C:, where R = hydrogen, alkyl, halogen.

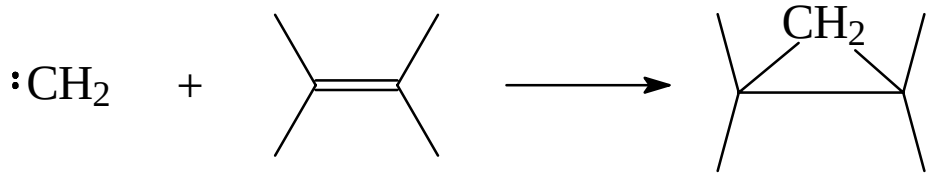
The simplest carbene is methylene aka carbene:



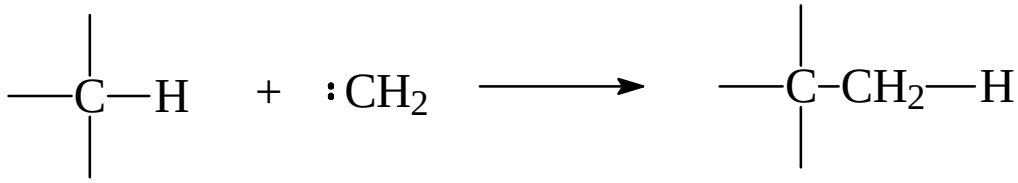
diazomethane

Methylene is highly reactive; it can add to double bonds to make a cyclopropane ring, but it can also insert itself into C-H bonds, resulting in low yields for the addition.

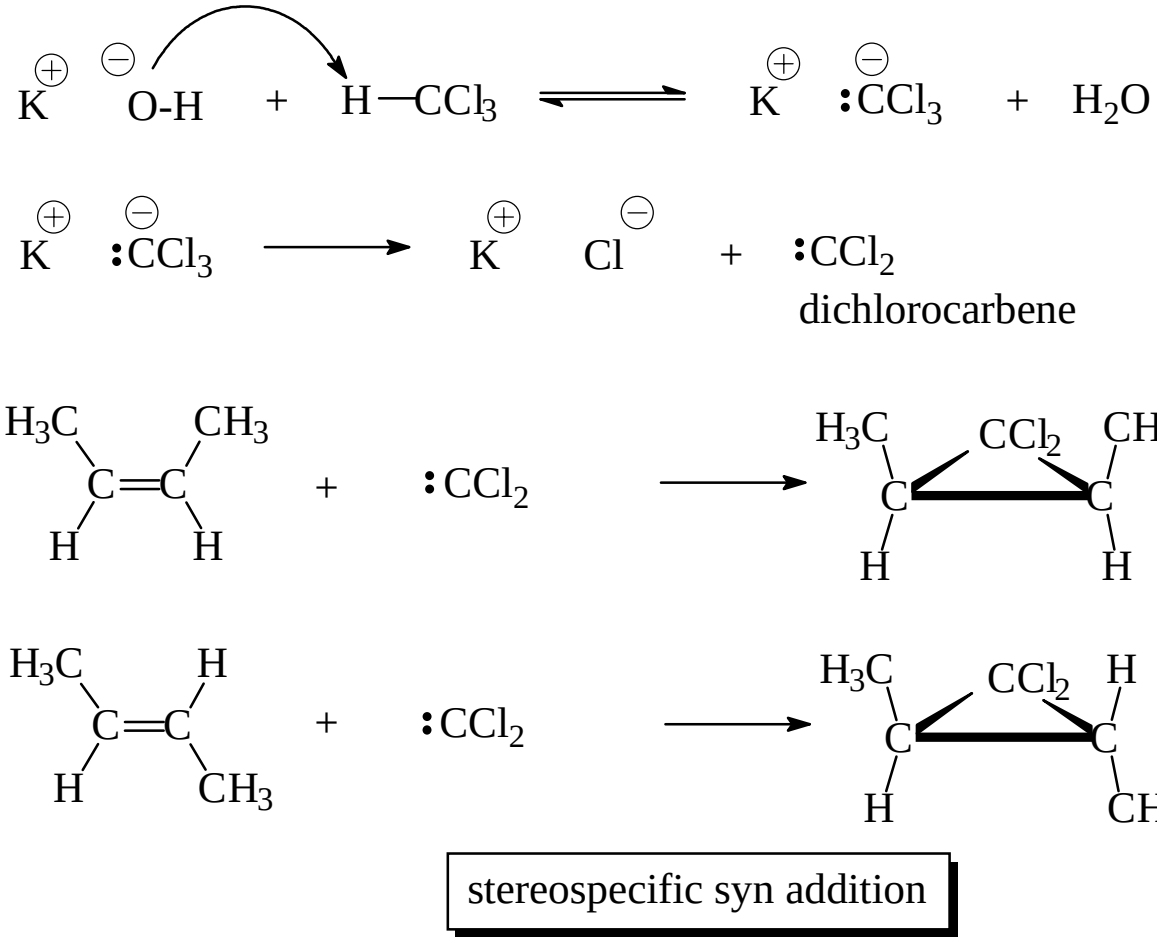
Addition ---



Insertion ---

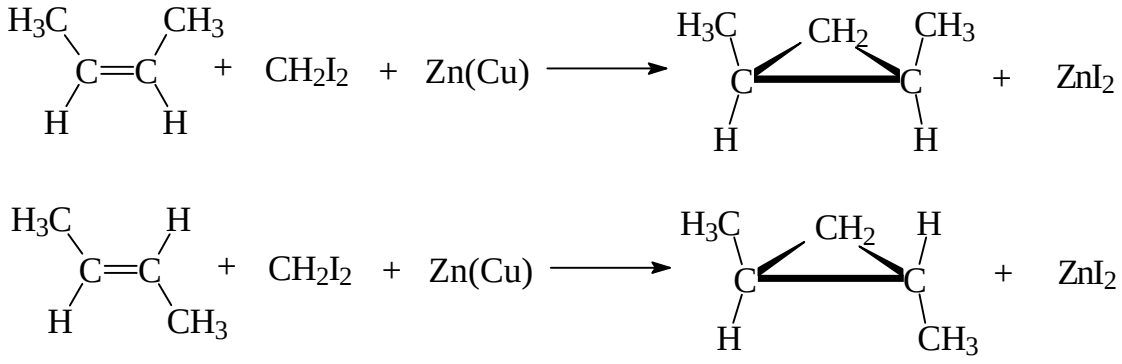


Addition of Dichlorocarbene to an Alkene to Give a Dichlorocyclopropane ---



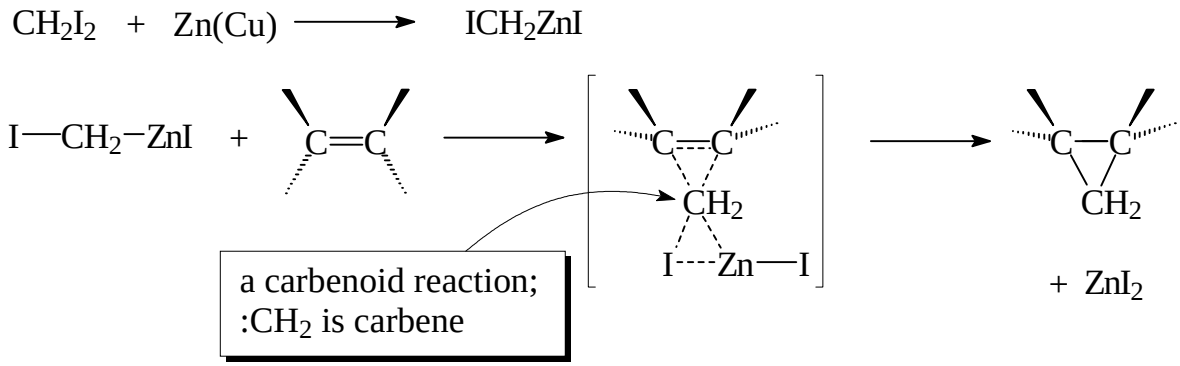
This reaction is stereospecific and syn.

Simmons-Smith Reaction: Alkene to Cyclopropane ---



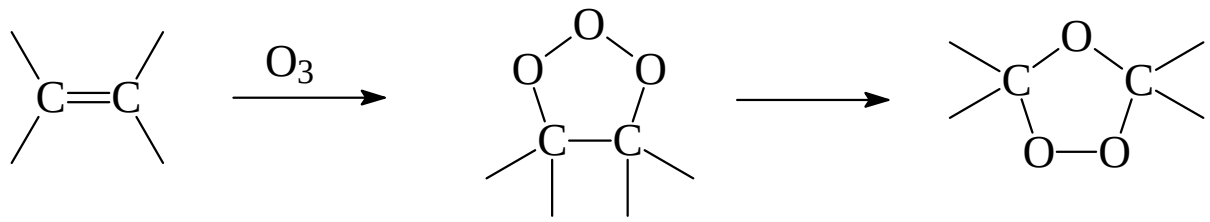
stereospecific syn addition

Mechanism:

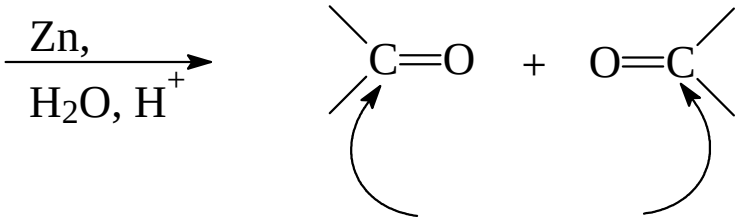


This reaction gives a cyclopropane ring cleanly; σ-bond insertion is not a problem here.

Ozonolysis: Structure Determination by Degradation ---



a molozonide an ozonide



aldehydes & ketones

These carbons
were joined
by a double bond.