Alkenes - Addition Reactions

Alkenes- reactions.

Addition

Ionic

Free radical

Reduction

Oxidation

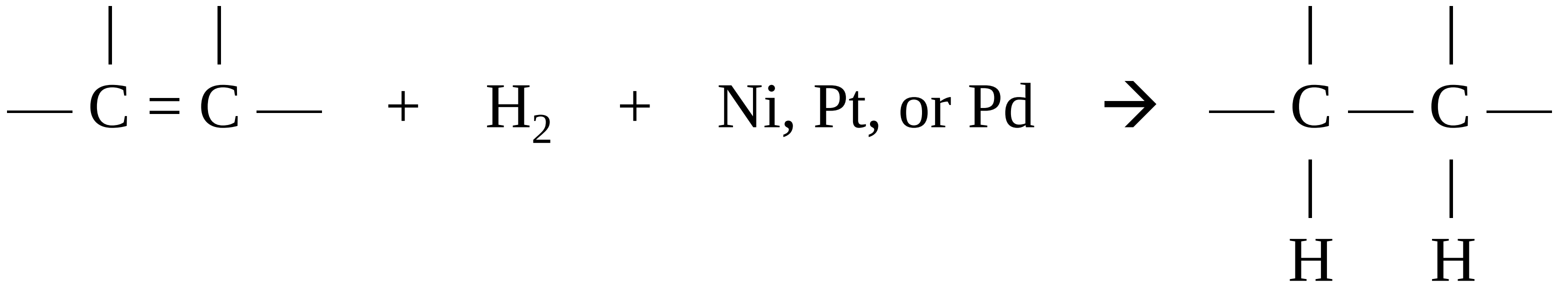
Substitution

Reactions, alkenes:

1. **Addition of hydrogen (reduction).**
2. **Addition of halogens.**
3. **Addition of hydrogen halides.**
4. **Addition of sulfuric acid.**
5. **Addition of water (hydration).**
6. **Addition of aqueous halogens (halohydrin formation).**
7. **Dimerization.**
8. **Alkylation.**

9. Oxymercuration-demercuration.
10. Hydroboration-oxidation.
11. Addition of free radicals.
12. Polymerization.
13. Addition of carbenes.
14. Epoxidation.
15. Hydroxylation.
16. Allylic halogenation
17. Ozonolysis.
18. Vigorous oxidation.

1. Addition of hydrogen (reduction).



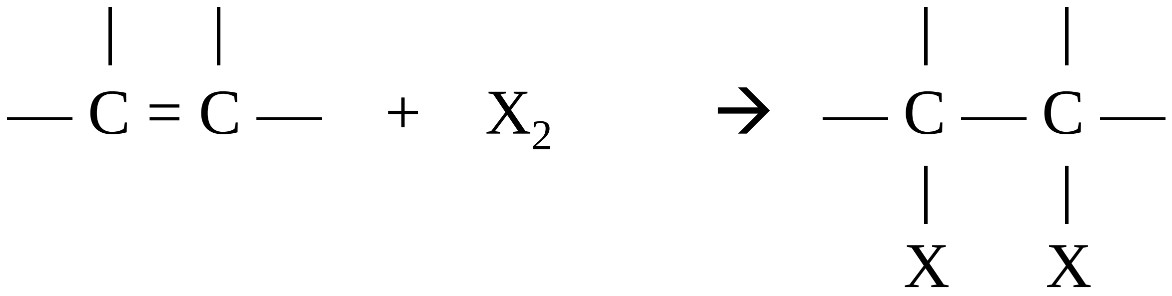
a) Requires catalyst.

b) #1 synthesis of alkanes

$$CH_3CH{=}CHCH_3 \quad + \quad H_2, \text{Ni} \rightarrow \quad CH_3CH_2CH_2CH_3$$

2-butene   *n*-butane

2) Addition of halogens.



a) $X_2 = Br_2$ or Cl_2

b) test for unsaturation with Br_2

$$CH_3CH_2CH{=}CH_2 \quad + \quad Br_2/CCl_4 \quad \rightarrow \quad CH_3CH_2\underset{Br}{C}H\underset{Br}{C}H_2$$

1-butene — 1,2-dibromobutane

3. Addition of hydrogen halides.

$$-\overset{|}{C}=\overset{|}{C}- \quad + \quad HX \rightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}-$$

a) HX = HI, HBr, HCl

b) Markovnikov orientation

$$CH_3CH{=}CH_2 \quad + \quad HI \rightarrow CH_3\underset{I}{CH}CH_3$$

$$CH_2\overset{CH_3}{C}{=}CH_2 \quad + \quad HBr \rightarrow CH_3\underset{Br}{\overset{CH_3}{C}}CH_3$$

Markovnikov's Rule:

In the addition of an acid to an alkene the hydrogen will go to the vinyl carbon that already has the greater number of hydrogens.

$$CH_3CH_2CH{=}CH_2 \quad + \quad HCl \quad \rightarrow \quad CH_3CH_2\underset{\displaystyle Cl}{C}HCH_3$$

$$CH_3CH{=}\overset{\displaystyle CH_3}{C}CH_3 \quad + \quad HBr \quad \rightarrow \quad CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}CH_3$$

$$CH_3CH{=}CHCH_3 \quad + \quad HI \quad \rightarrow \quad CH_3CH_2\underset{\displaystyle I}{C}HCH_3$$

An exception to Markovikov’s Rule:

$CH_3CH{=}CH_2$ + HBr, peroxides → $CH_3CH_2CH_2Br$

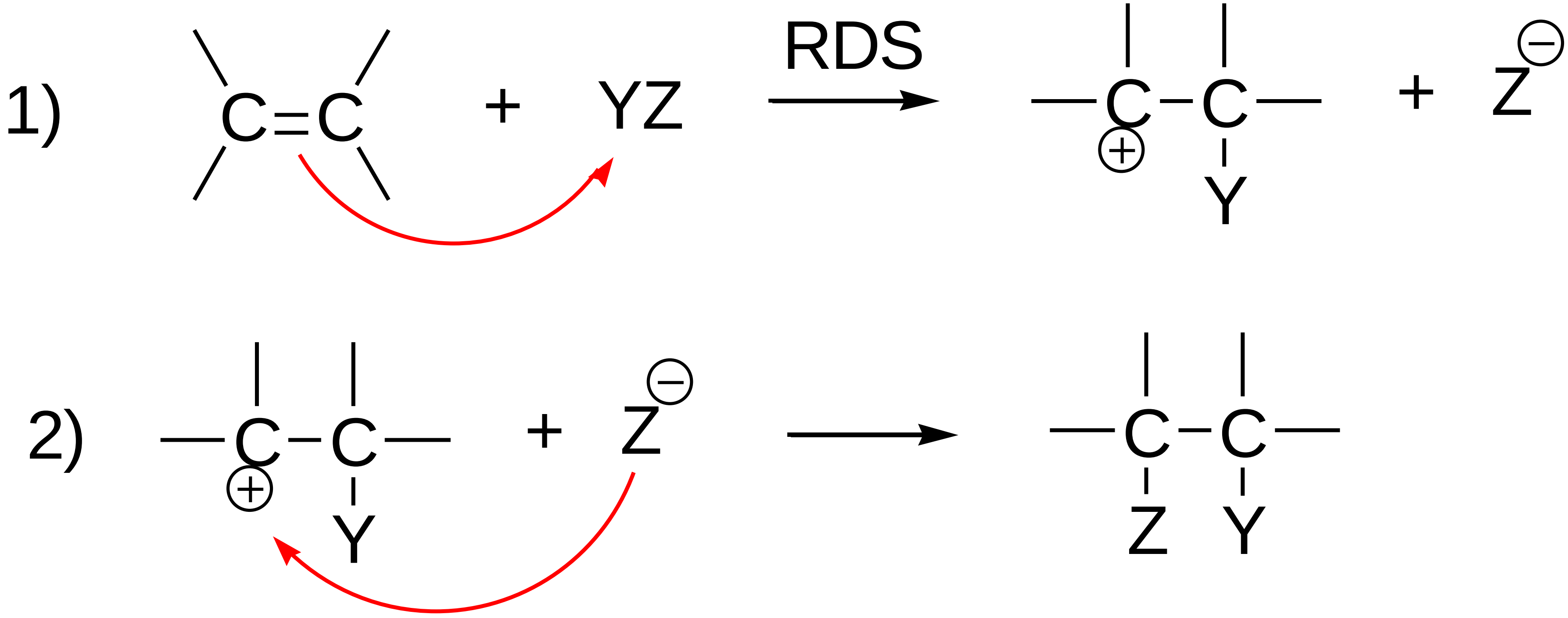
$\quad\quad CH_3 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$

$CH_3C{=}CH_2$ + HBr, peroxides → CH_3CHCH_2Br

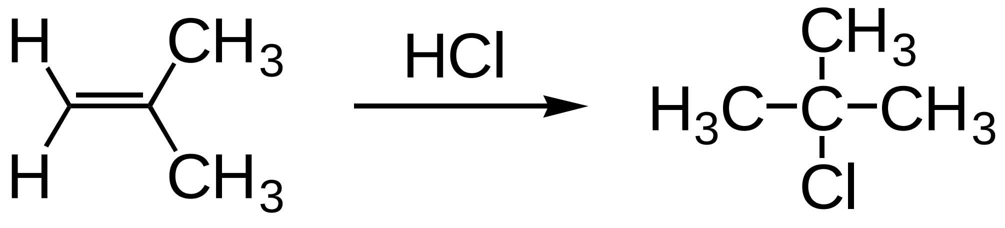
“anti-Markovnikov” orientation

note: this is only for HBr.

Ionic electrophilic addition mechanism



Markovnikov’s rule



In 1869, Markovnikov proposed that in the addition of an acid to an alkene, the hydrogen of the acid bonds to the carbon which is already bonded to the greater number of hydrogens.

Markovnikov's rule

$$CH_3CH_2CH{=}CHCH_3 + HI \longrightarrow$$

$$CH_3CH_2CHICH_2CH_3 + CH_3CH_2CH_2CHICH_3$$

Each carbon of the double bond is bonded to one H therefore both isomers are formed.

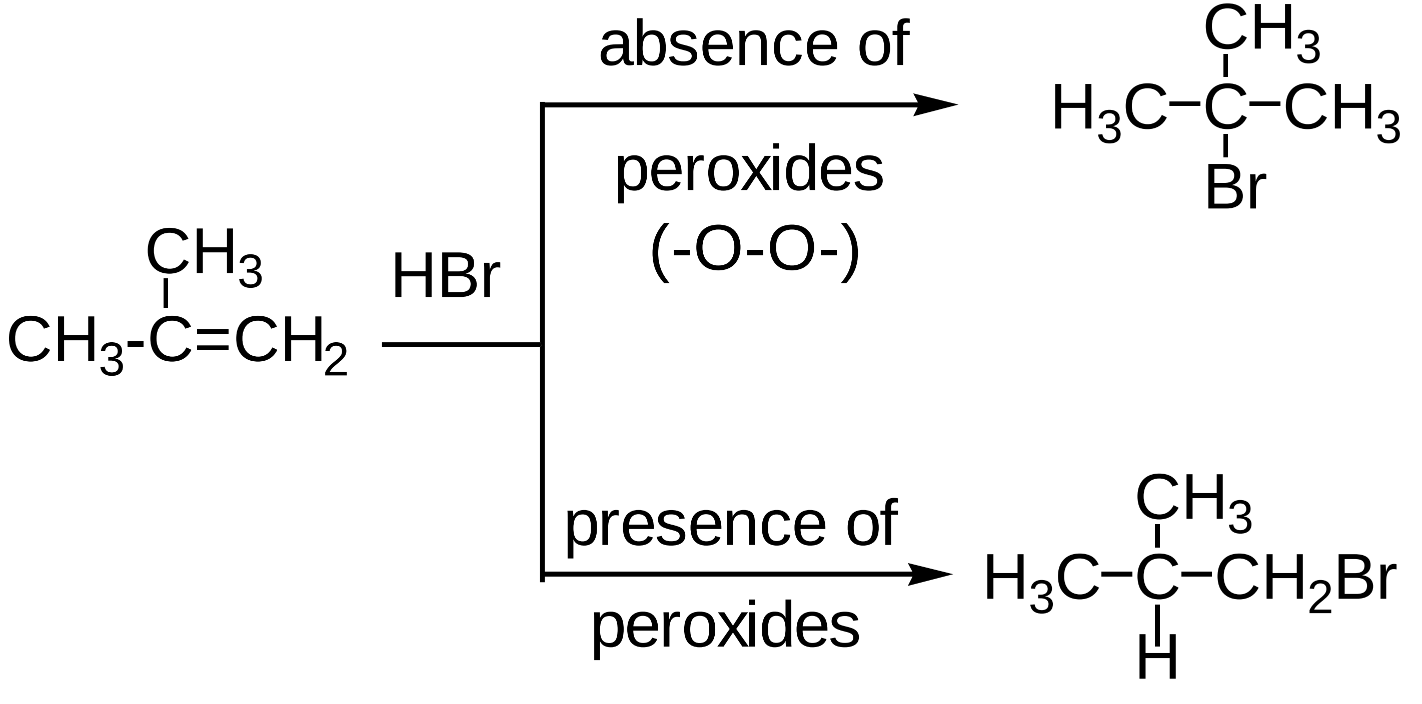
Markovnikov addition - a regioselective reaction

These reactions are said to be **regioselective** because only one of the two possible directions of addition occurs.

Regioselectivity - the preferential formation of one isomer in those situations where a choice is possible.

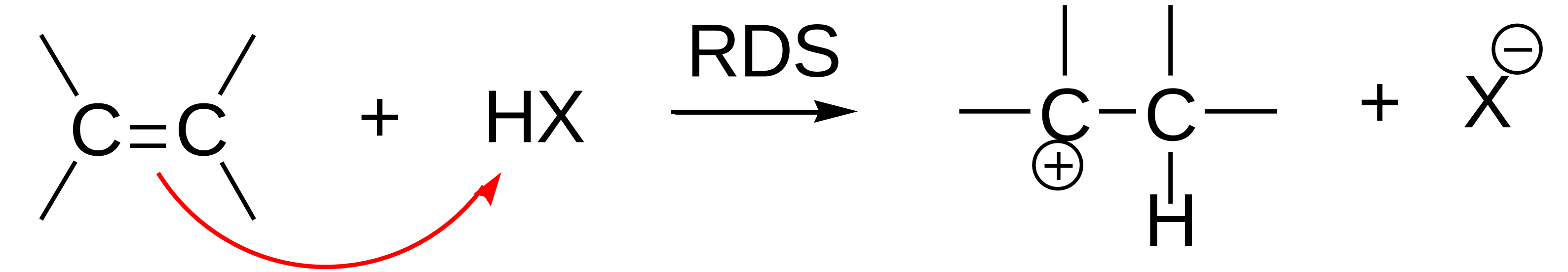
HBr - the peroxide effect

1933, Kharasch and Mayo

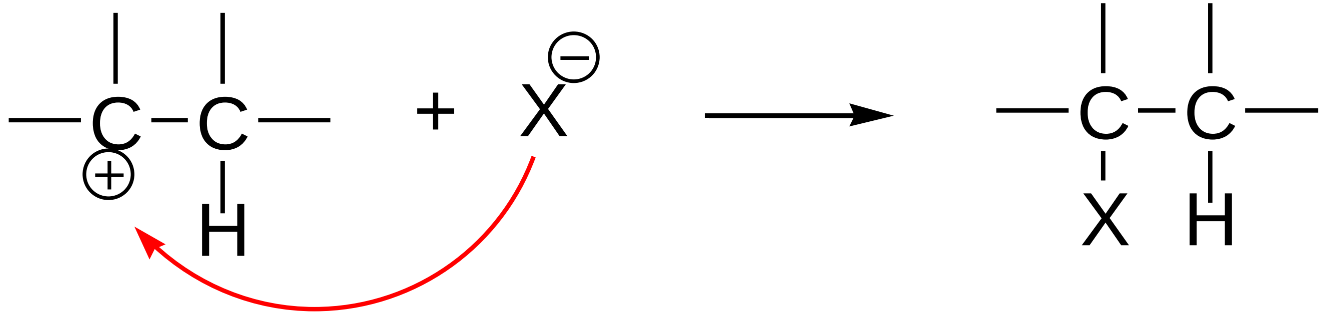


mechanism for addition of HX

1)



2)



why Markovinkov?

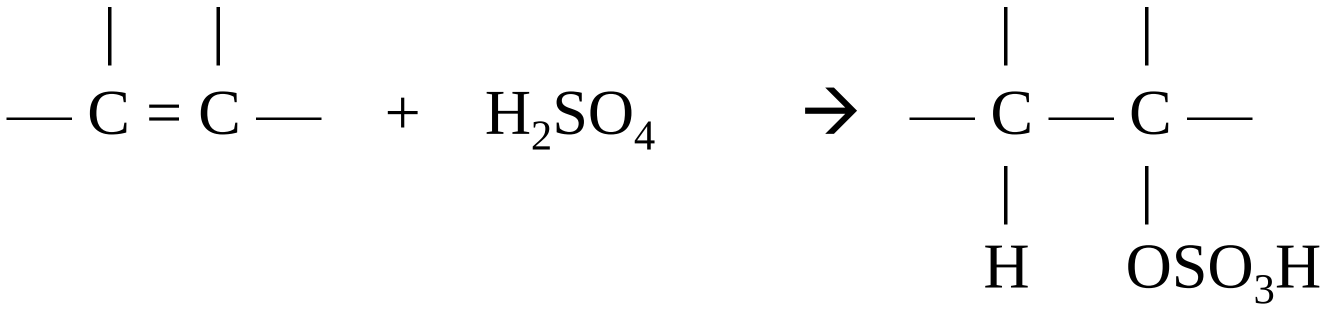
$CH_3CH{=}CH_2$ + HBr → CH_3CHCH_2 (with H below the middle C and + on the end C; struck through) — 1° carbocation ☹

or? CH_3CHCH_2 (with + on the middle C and H below the end C) — 2° carbocation more stable

+ Br^- → CH_3CHCH_3 (with Br below the middle C)

In ionic electrophilic addition to an alkene, the electrophile always adds to the carbon-carbon double bond so as to form the more stable carbocation.

4. Addition of sulfuric acid.



alkyl hydrogen sulfate

Markovnikov orientation.

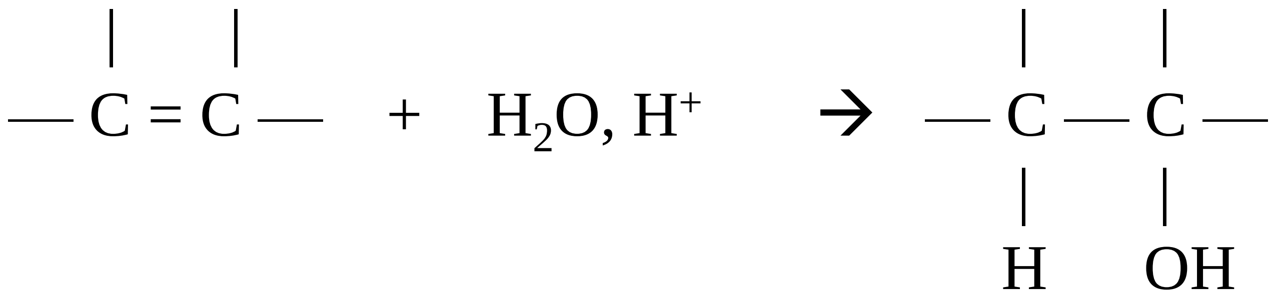
$CH_3CH{=}CH_2$ + H_2SO_4 → CH_3CHCH_3

O

O-S-O

OH

5. Addition of water.



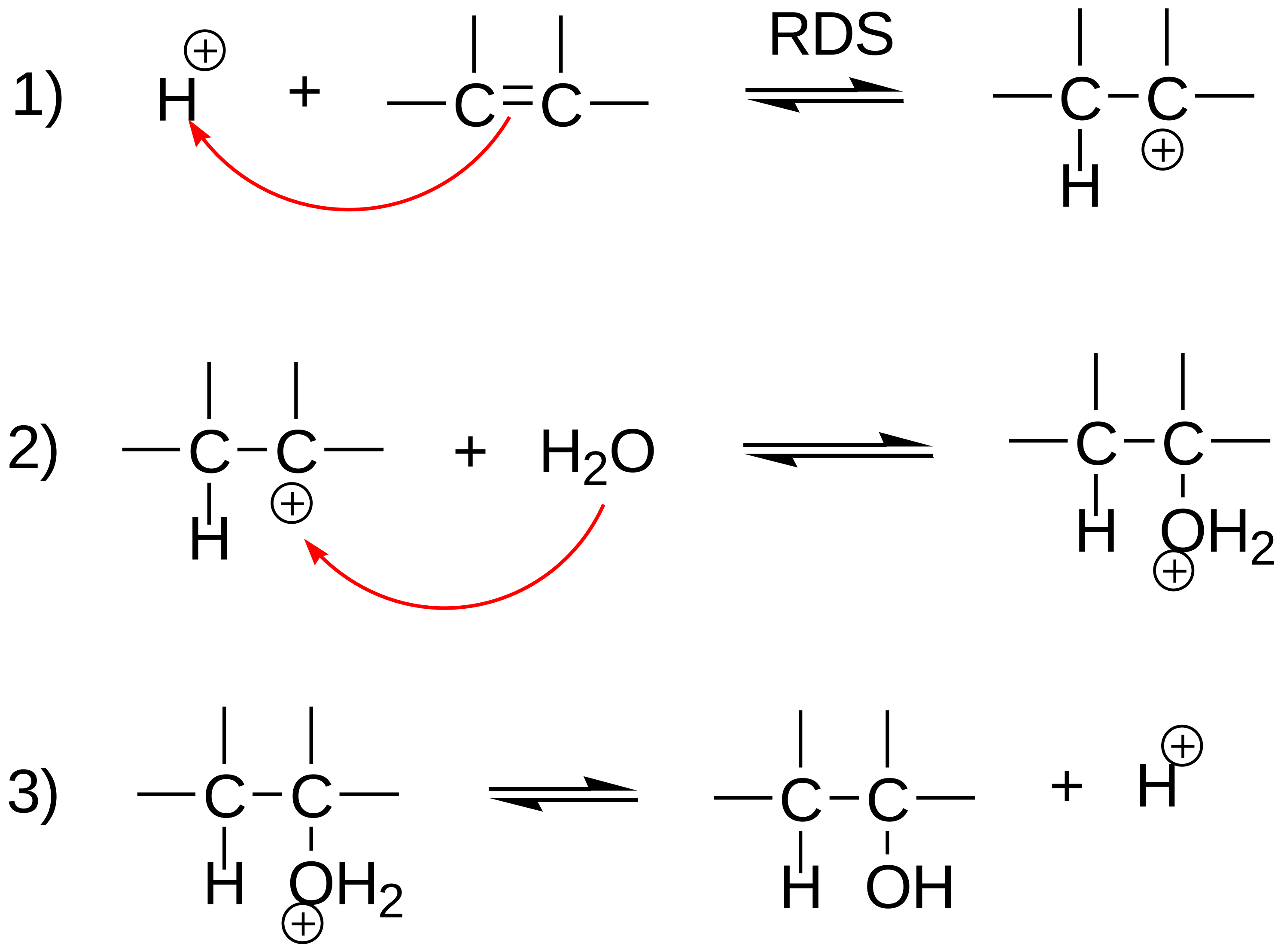
a) **requires acid**

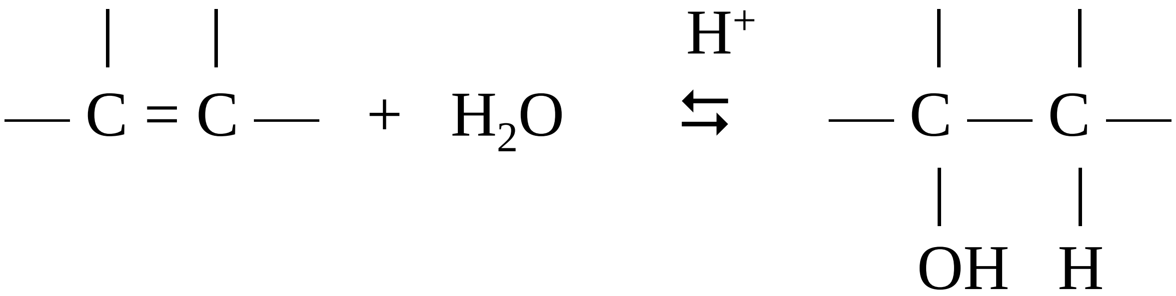
b) **Markovnikov orientation**

c) **low yield** ☹

$$CH_3CH_2CH{=}CH_2 \quad + \quad H_2O,\ H^+ \quad \rightarrow \quad CH_3CH_2\underset{\displaystyle OH}{CH}CH_3$$

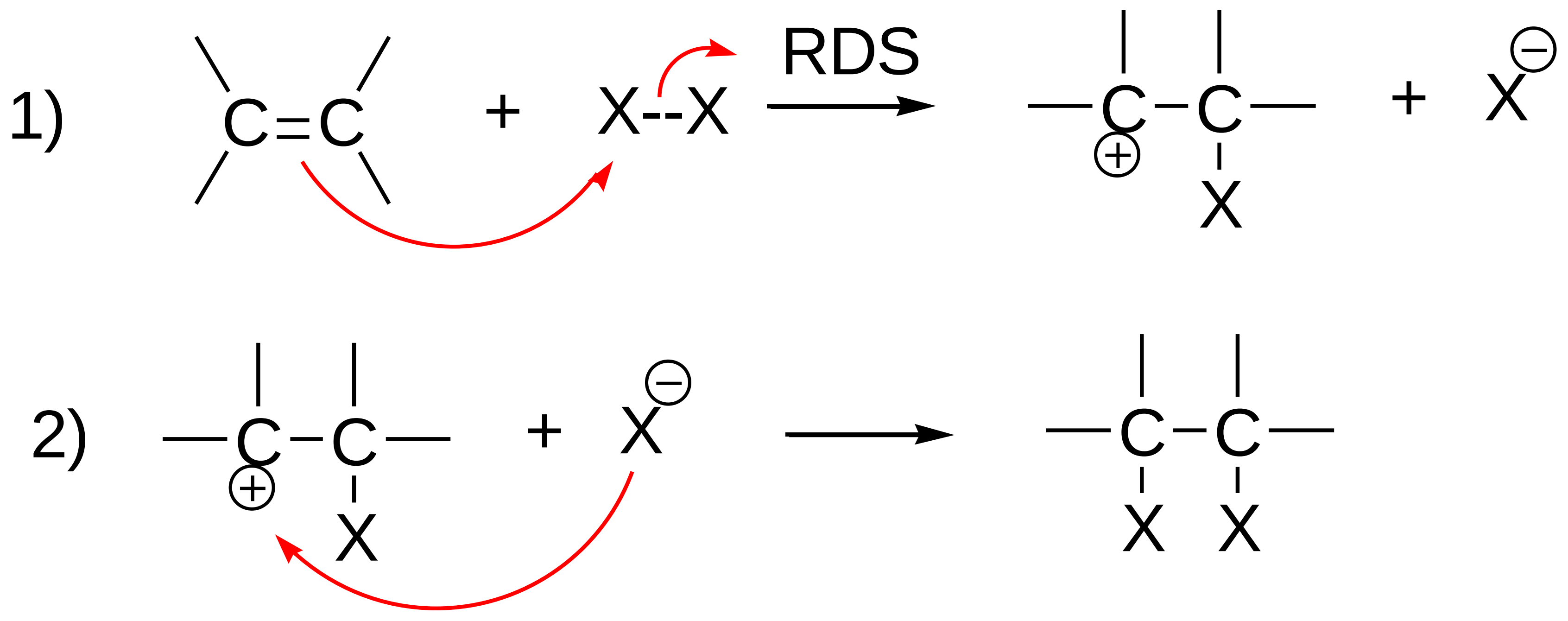
Mechanism for addition of water



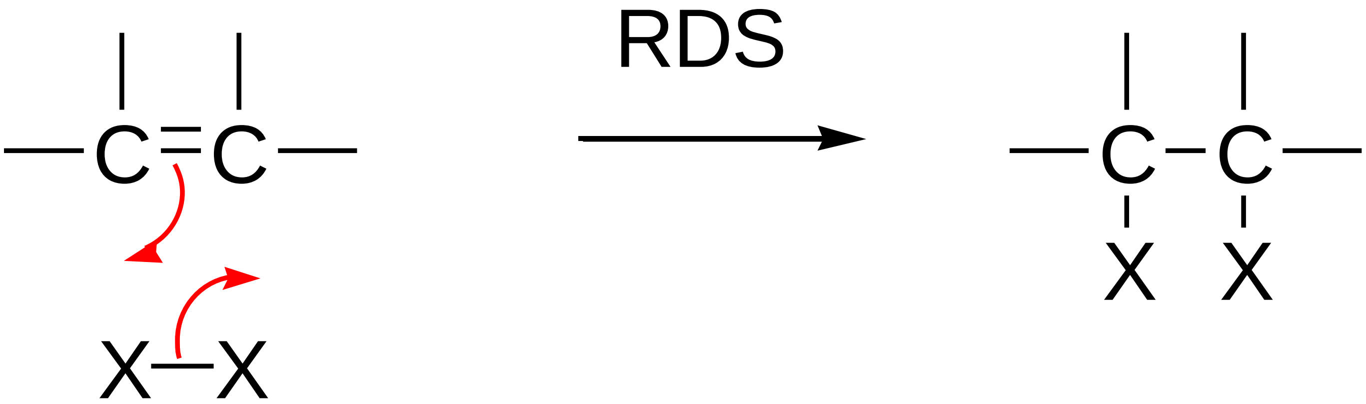


Mechanism for addition of water to an alkene to form an alcohol is the exact reverse of the mechanism (E1) for the dehydration of an alcohol to form an alkene.

mechanism for addition of X_2

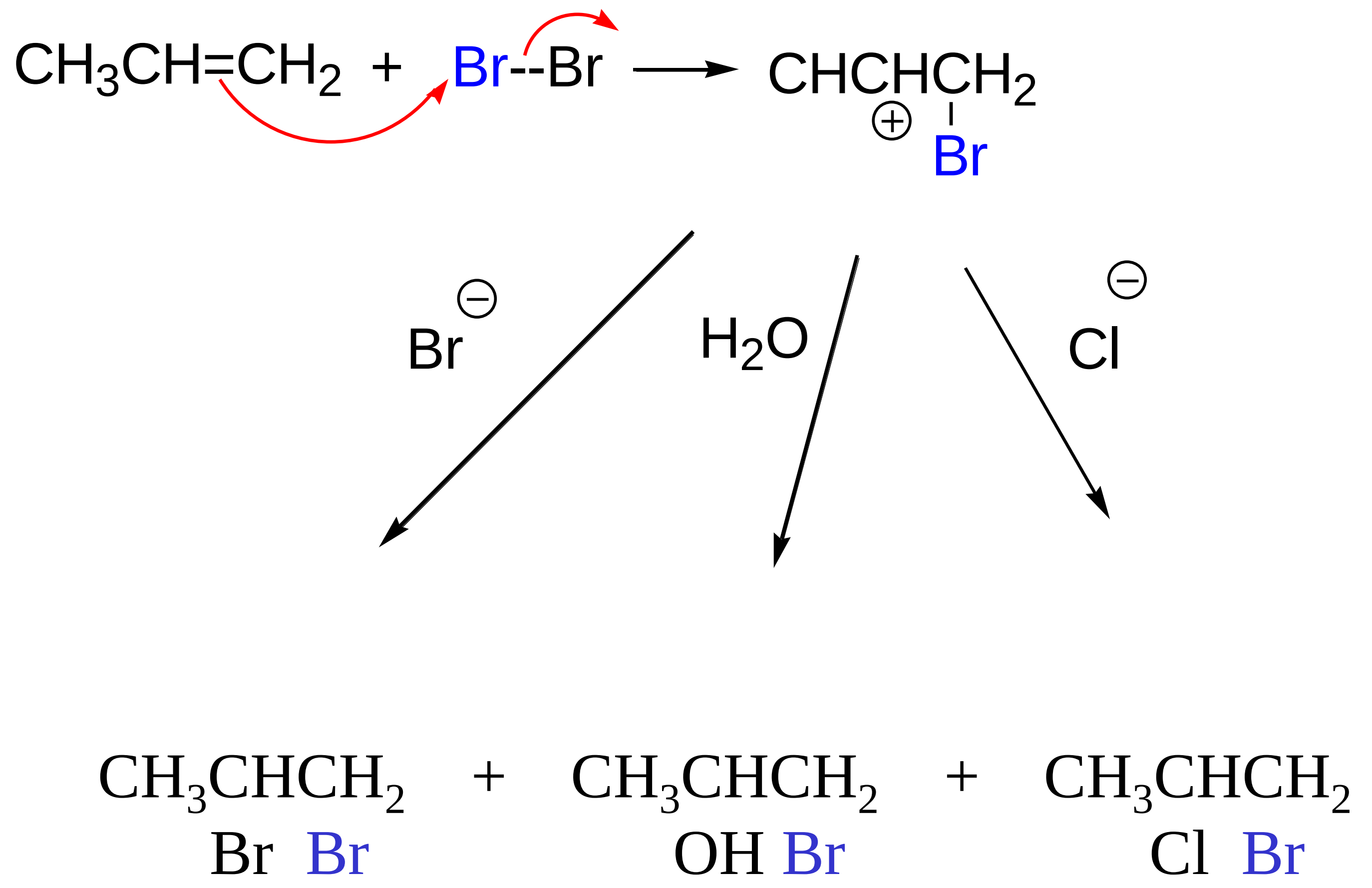


How do we know that the mechanism isn't this way?



One step, concerted, no carbocation

$$CH_3CH{=}CH_2 + Br_2 + H_2O + NaCl \rightarrow$$



6. Addition of halogens + water (halohydrin formation):

$$-\overset{|}{C}=\overset{|}{C}- \quad + \quad X_2,\ H_2O \ \rightarrow \ -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- \quad + \quad HX$$

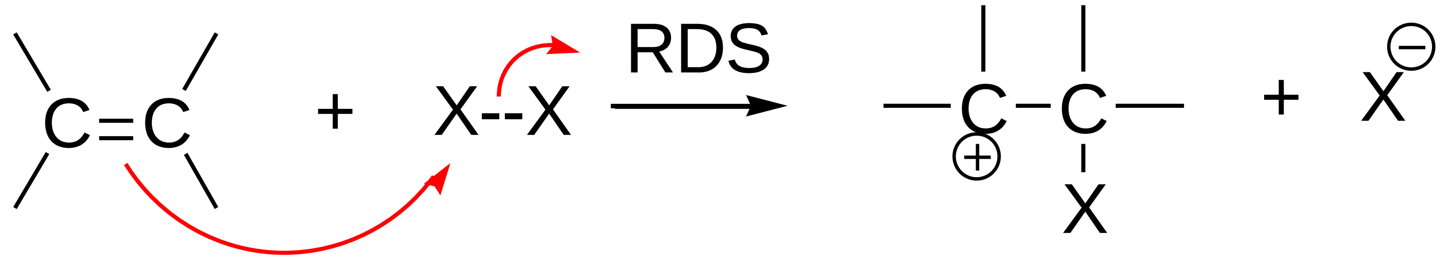
a) $X_2 \; = \; Br_2, Cl_2$

b) Br_2 = electrophile

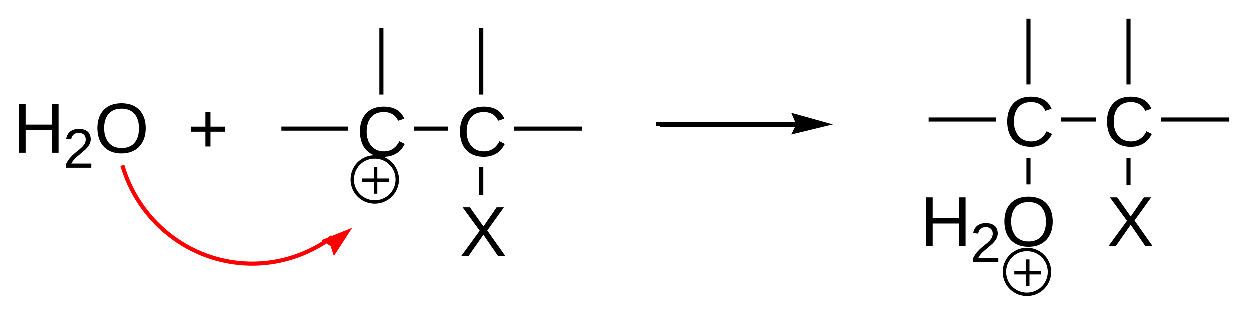
$$CH_3CH{=}CH_2 \quad + \quad Br_2(aq.) \ \rightarrow \ CH_3\underset{OH}{CH}\underset{Br}{CH_2} \quad + \quad HBr$$

mechanism for addition of $X_2 + H_2O$

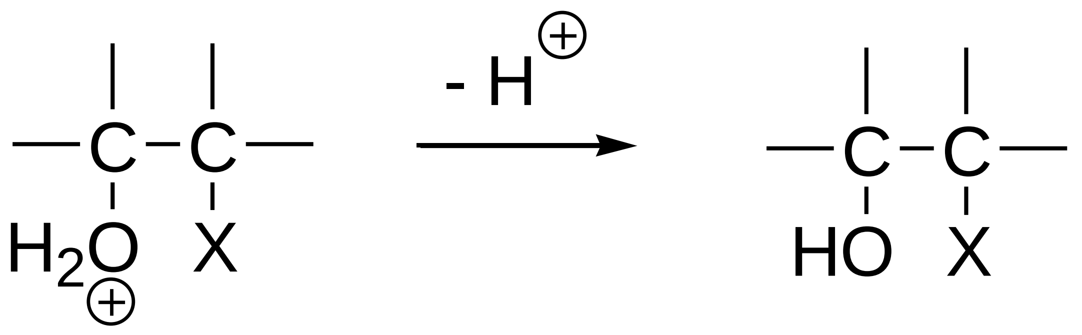
1)



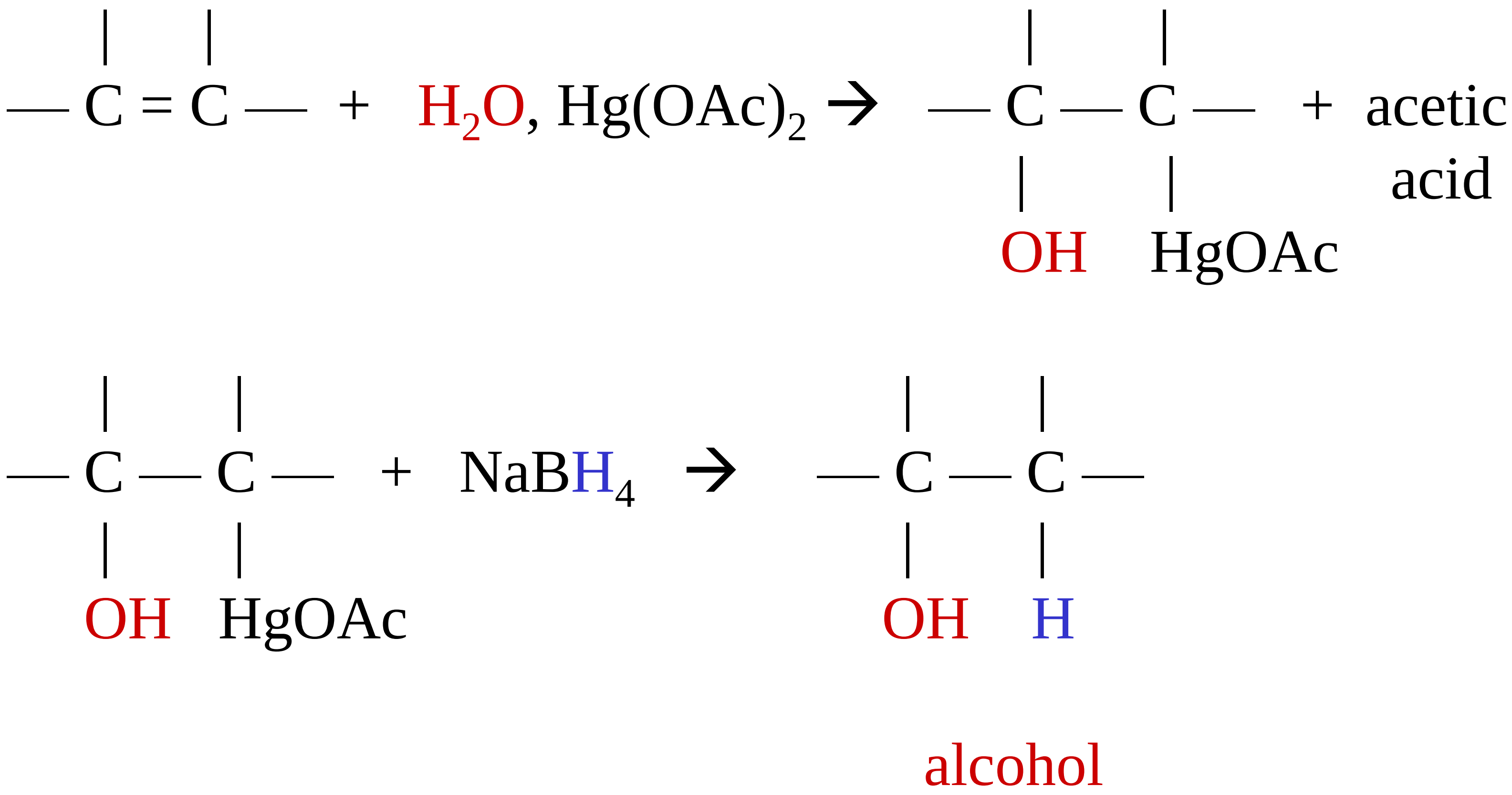
2)



3)



9. Oxymercuration-demercuration.



Oxymercuration-demercuration:

a) **#1 synthesis of alcohols.**

b) **Markovnikov orientation.**

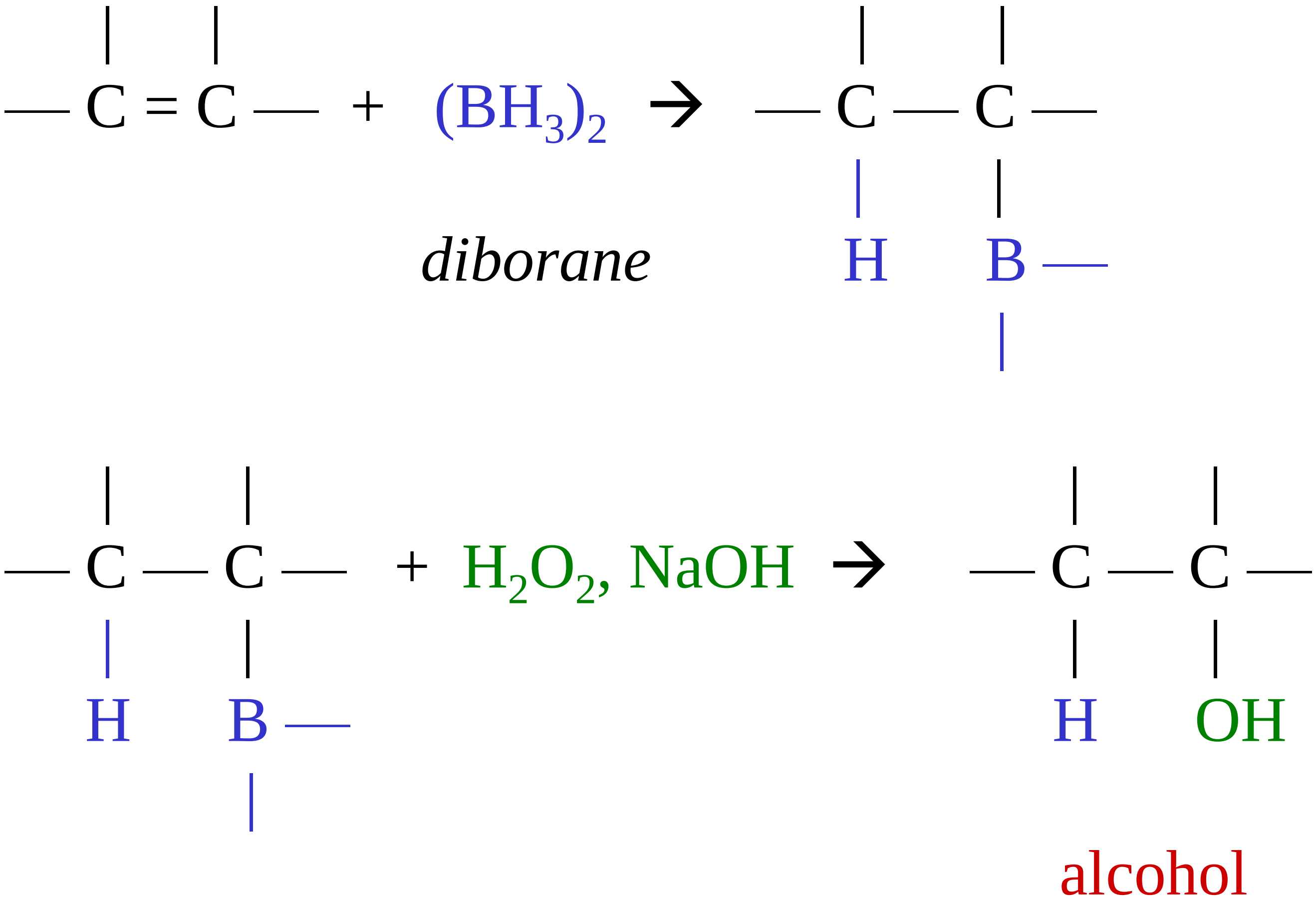
c) **100% yields.** ☺

d) **no rearrangements** ☺

$CH_3CH_2CH{=}CH_2$ + H_2O, $Hg(OAc)_2$; then $NaBH_4$ →

$$\underset{\text{OH}}{CH_3CH_2\underset{|}{C}HCH_3}$$

10. Hydroboration-oxidation.



Hydroboration-oxidation:

a) Synthesis of alcohols.

b) <u>Anti-Markovnikov</u> orientation. ✯

c) 100% yields. ☺

d) no rearrangements ☺

$CH_3CH_2CH{=}CH_2$ + $(BH_3)_2$; then H_2O_2, NaOH →

$CH_3CH_2CH_2CH_2$-OH

$$\begin{array}{l} \quad\ CH_3 \\ CH_3C{=}CH_2 \end{array} \quad + \quad H_2O,\ Hg(OAc)_2;\ \text{then}\ NaBH_4 \ \rightarrow$$

Markovnikov

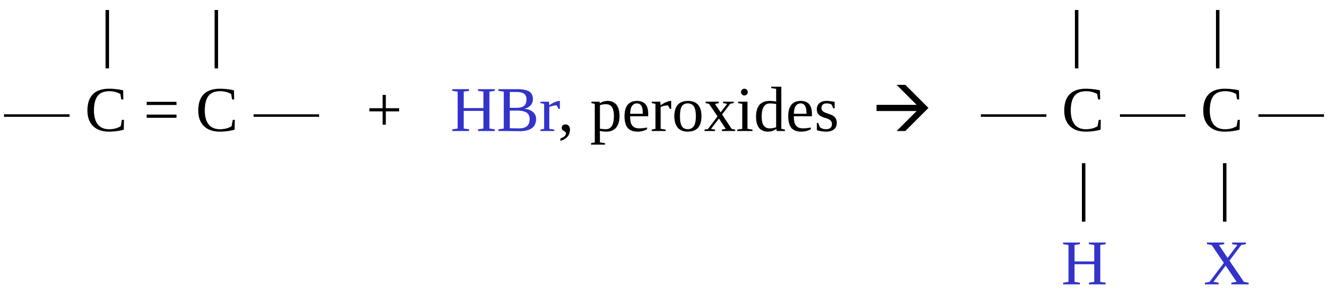
$$\begin{array}{c} CH_3 \\ CH_3CCH_3 \\ OH \end{array}$$

$$\begin{array}{l} \quad\ CH_3 \\ CH_3C{=}CH_2 \end{array} \quad + \quad (BH_3)_2;\ \text{then}\ H_2O_2,\ NaOH \ \rightarrow$$

anti-Markovnikov

$$\begin{array}{l} \quad\quad CH_3 \\ CH_3CHCH_2 \\ \quad\quad\quad\ OH \end{array}$$

11. Addition of free radicals.

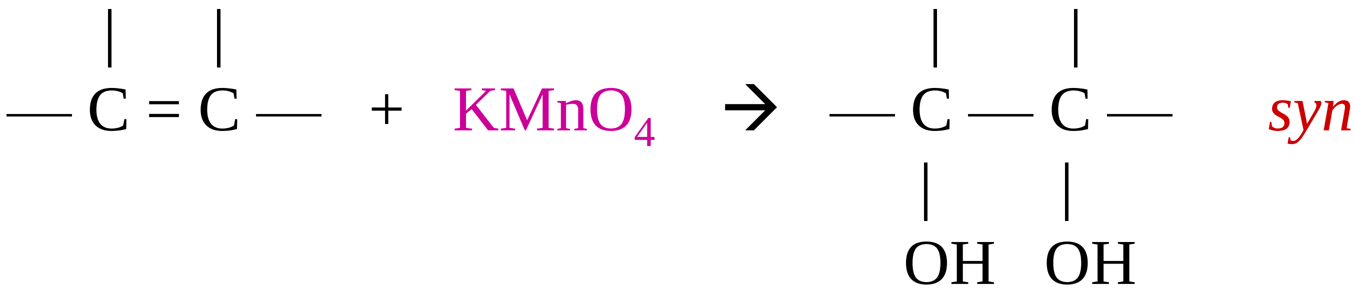


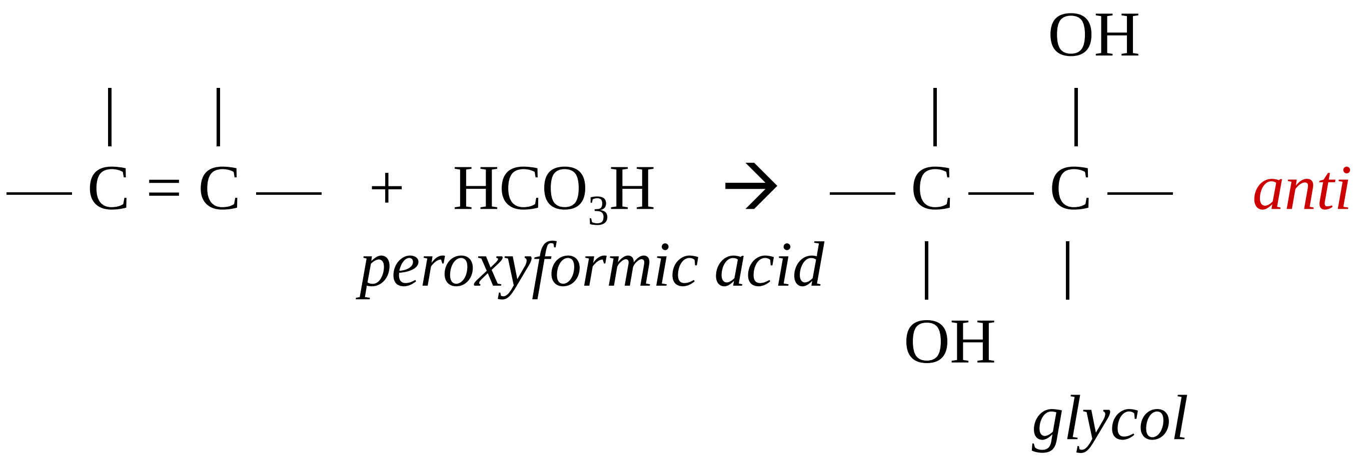
a) anti-Markovnikov orientation.

b) free radical addition

$CH_3CH{=}CH_2$ + HBr, peroxides → $CH_3CH_2CH_2\text{-}Br$

15. Hydroxylation. (mild oxidation)





$CH_3CH{=}CHCH_3 \quad + \quad KMnO_4 \quad \rightarrow \quad CH_3CH\text{-}CHCH_3$

OH OH

2,3-butanediol

Test for unsaturation* purple $KMnO_4$ → brown MnO_2

$CH_2{=}CH_2 \quad + \quad KMnO_4 \quad \rightarrow \quad CH_2CH_2$

OH OH

ethylene glycol

"anti-freeze"

17. Ozonolysis.

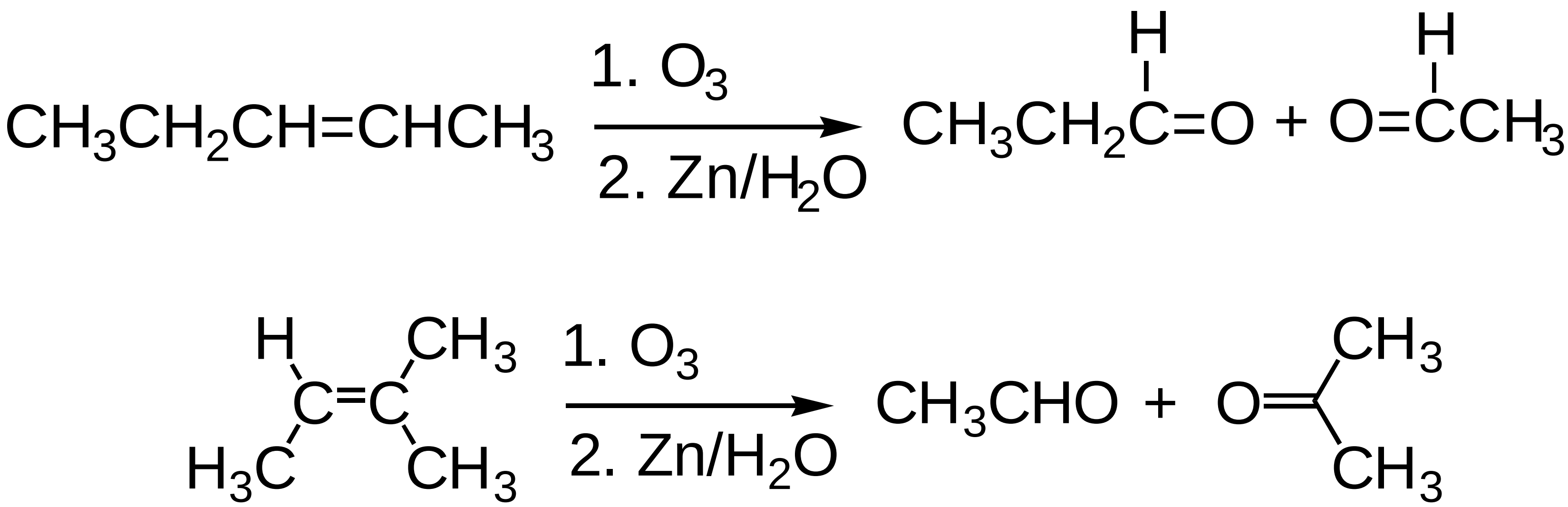
$$—\overset{|}{C}=\overset{|}{C}— \quad + \quad O_3\text{; then Zn, } H_2O \rightarrow —\overset{|}{C}=O \quad + \quad O=\overset{|}{C}—$$

used for identification of alkenes

$$CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_3 \quad + \quad O_3\text{; then Zn, } H_2O \rightarrow$$

$$CH_3CH_2CH{=}O \quad + \quad O{=}\overset{CH_3}{\overset{|}{C}}CH_3$$

Ozonolysis


CH3CH2CH=CHCH3
1. O3
2. Zn/H2O
H
CH3CH2C=O + O=CCH3
H
H
C=C
CH3
H3C
CH3
1. O3
2. Zn/H2O
CH3CHO +
O
CH3
CH3