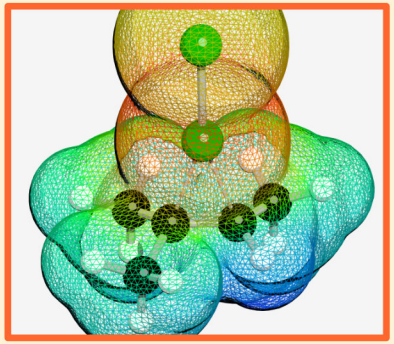
HIGHLIGHTS

- Hydrohalogenation - proton transfer and nucleophilic attack
- Bromination and bromohydrin formation - bromonium formation and nucleophilic attack
- Epoxidation - concerted addition and alternative curly arrow mechanism
- Factors influencing reactivity - stability of carbocations, nucleophilicity and regioselectivity of bromonium ring opening



The last one page handout covered electrophilic addition to alkenes (but not methods that gave *anti*-Markovnikov addition). It should have been suitable for revision and early organic chemistry courses.

This handout covers the same material but presents the 'frontier' molecular orbital overview. This helps organic chemists rationalize experimental observations. It is a halfway point between the simplicity of curly arrows and the accurate, but complex, true molecular orbital approach.

As always, I hope it is of use to some of you.

CHEMISTRY CLASSICS

π NUCLEOPHILES PART 2

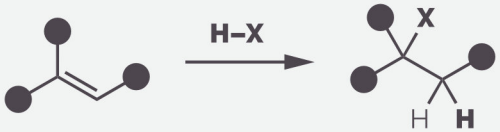
'FRONTIER' MOLECULAR ORBITALS

Molecular orbitals & alkenes

Making MOLECULES
www.makingmolecules.com

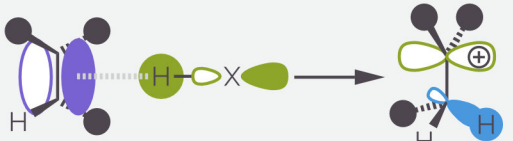
1. Hydrohalogenation

General reaction



control of **regiochemistry**
(stabilization of carbocation)

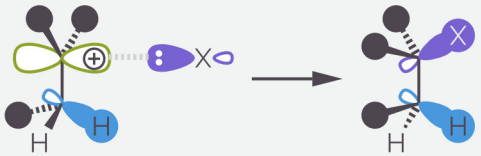
Step 1: proton transfer



HOMO π orbital
LUMO σ* antibonding orbital
new bond σ bond

Step 2: nucleophilic addition

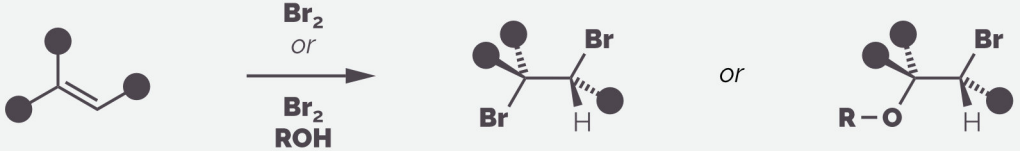
LUMO empty 2p orbital
HOMO non-bonding orbital



nucleophile can approach either face

2. Bromination & bromohydrin formation

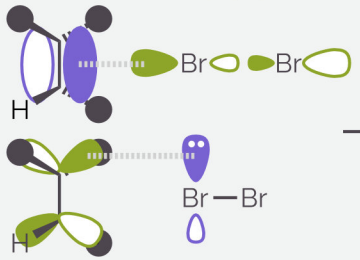
General reaction



control of **regiochemistry** (stabilization of δ+)
control of **stereochemistry** (*anti*-addition)

Step 1: bromonium formation

HOMO π orbital
LUMO σ* antibonding orbital

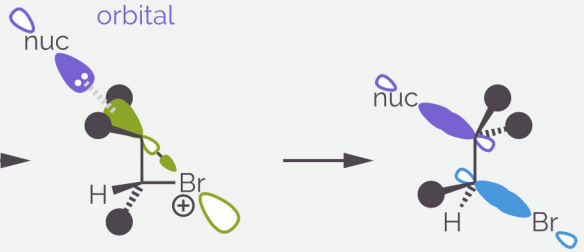


secondary interaction π* antibonding orbital
secondary interaction non-bonding lone pair

concerted reaction
2 x C–Br formed as C=C breaks

Step 2: nucleophilic attack

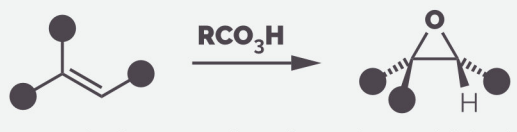
HOMO non-bonding orbital
LUMO σ* antibonding orbital



nucleophile must approach *anti* C–Br
regioselectivity favors more stable δ+

3. Epoxidation

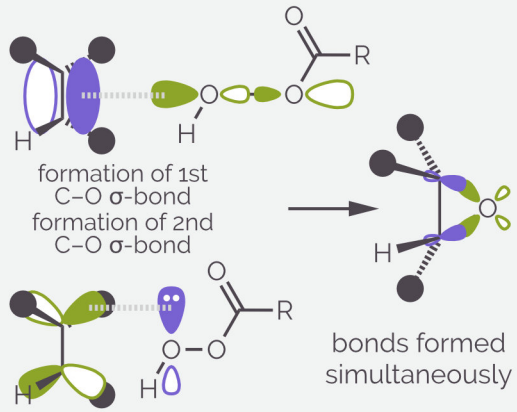
General reaction



control of **stereochemistry** (*syn* addition)

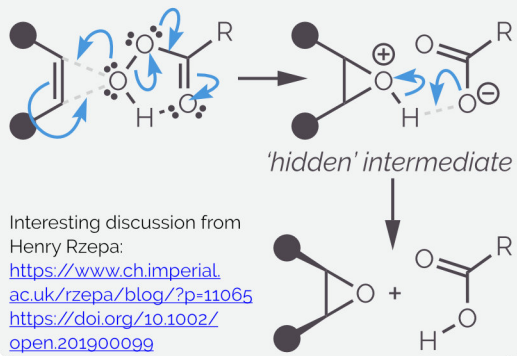
Concerted reaction

HOMO π orbital
LUMO σ* antibonding orbital



secondary interaction π* antibonding orbital
secondary interaction sp^3 lone pair

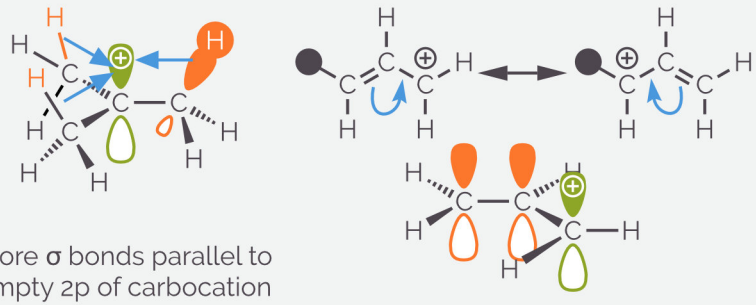
Is the 'textbook' mechanism wrong?



Interesting discussion from Henry Rzepa:
https://www.ch.imperial.ac.uk/rzepa/blog/?p=11065
https://doi.org/10.1002/open.201900099

4. Factors influencing reactivity

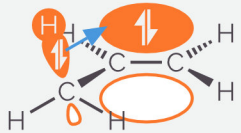
Stability of carbocations



more σ bonds parallel to empty 2p of carbocation more stable

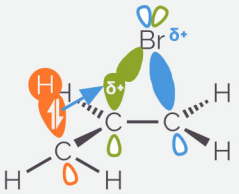
delocalization stabilizes carbocation

Increased nucleophilicity
more substituents = more reactive



interaction between **σ bond** & **π bond** raises **HOMO** - makes it more **nucleophilic**

Regioselectivity of attack on bromonium ion



more substituted **C** stabilizes δ+ better - **Br** starting to leave before attack