Course CHEM 343 Lecturer Sam Gellman

Day Wednesday Date 10/12/11

Notes Taken By Leslie Herndon Total # of Pages 4

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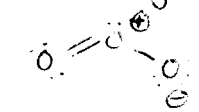
**DO NOT STAPLE**

* No office hour on Friday

## Ozonolysis of alkenes

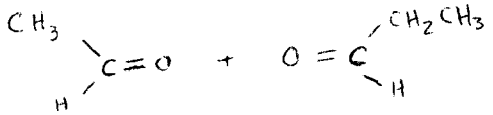
- lysis = breaking

- Ozonolysis = two step process with 2 variants (sometimes different products)

Ozone = $O_3$ 

very reactive

**Ex:** Variant * 1

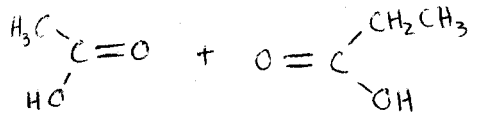
$CH_3-CH=CH-CH_2CH_3$ $\xrightarrow[2)\ (CH_3)_2S]{1)\ O_3}$ 

completely cleave C=C

$(CH_3-S-CH_3)$ thio ether

products = aldehydes

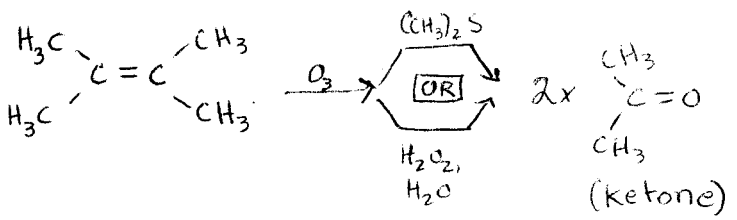
Variant * 2

$H_3C-CH=CHCH_2CH_3$ $\xrightarrow[2)\ H_2O_2, H_2O]{1)\ O_3}$ 

products = carboxylic acids

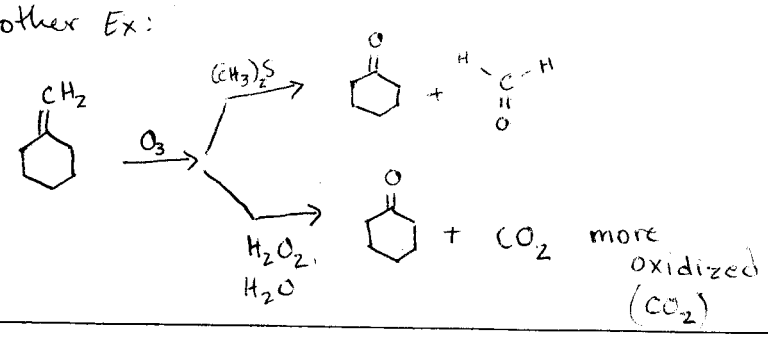
more oxidized

Another example:



* both variants give same products

Another Ex:



more oxidized ($CO_2$)

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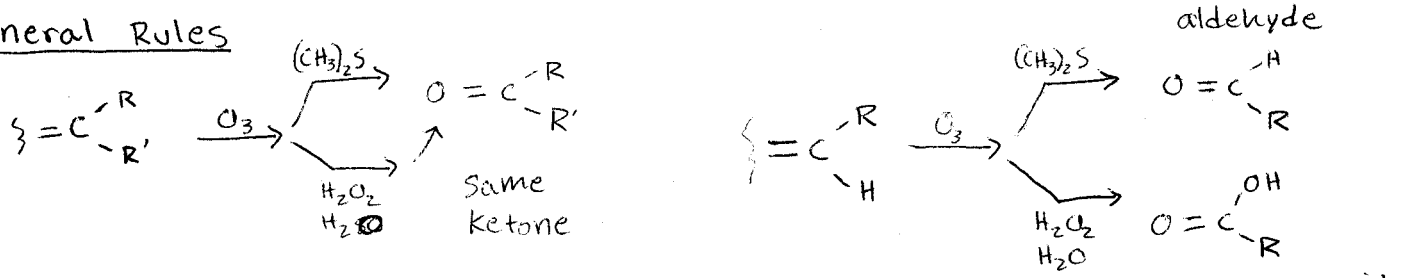
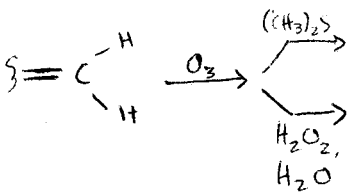
## General Rules

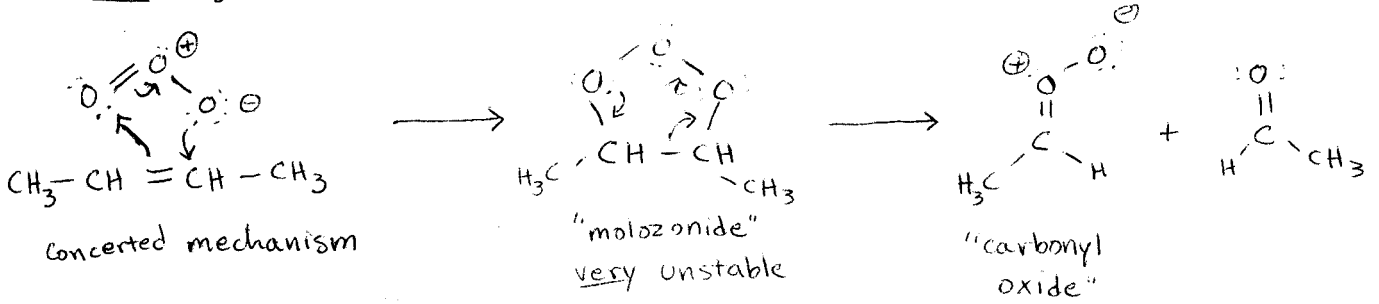


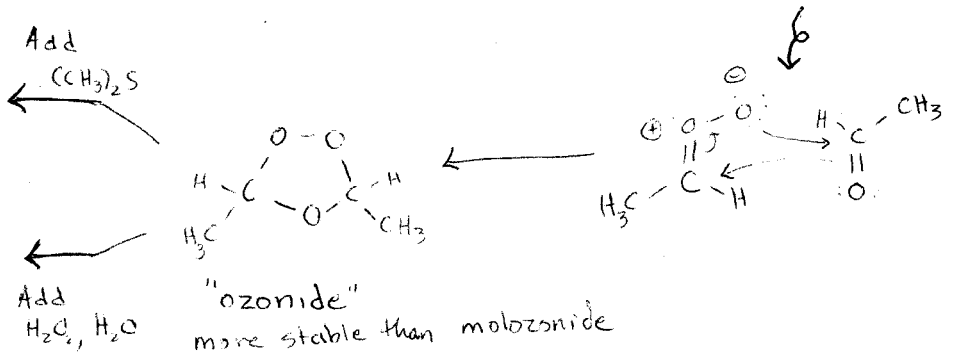




you fill in!

Historically widely used in analytical chemistry

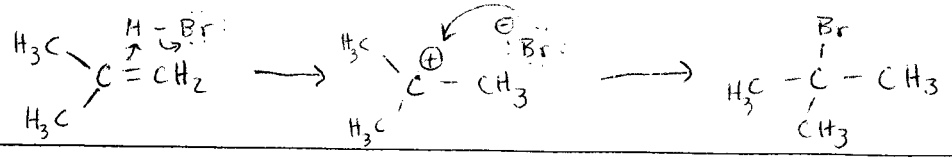
## Mechanism. $O_3$ rxn




## Anti-Markovnikov addn of HBr (only) to alkenes

recall: standard HX addn



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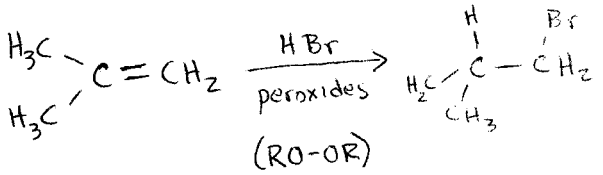
HOWEVER,



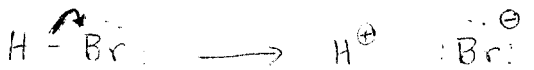

Peroxide impurities cause change in regioselectivity.
Change in mechanism - via radical intermediates

Radical species have unpaired electrons - reactive species b/c incomplete octet so looking for another e⁻ !

Two different ways to break bonds

1) Heterolysis - both electrons from the bonding pair go with 1 frag.

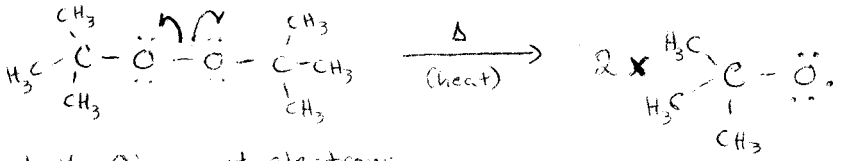
Ex.



all we've talked about so far.

2) Homolysis - each fragment takes one of e⁻ pair

Ex: ← half headed arrows for single e⁻ movement

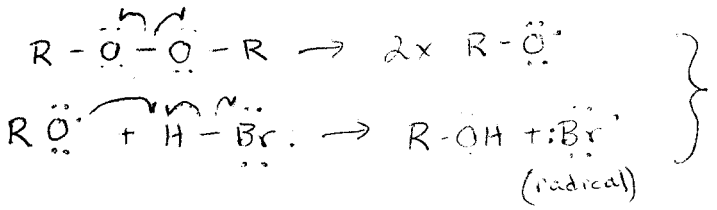



both O's want electrons

Radical!

(Note: half-arrow formalism)

Mech rationale for anti-Markovnikov HBr addn to alkenes



Initiation process
⇒ creation of radicals from non-radicals

:Br· then enters chain propagation cycle.

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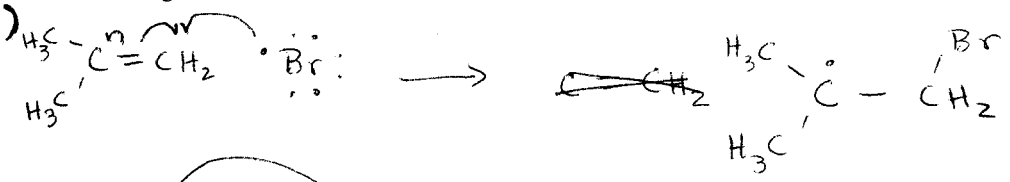
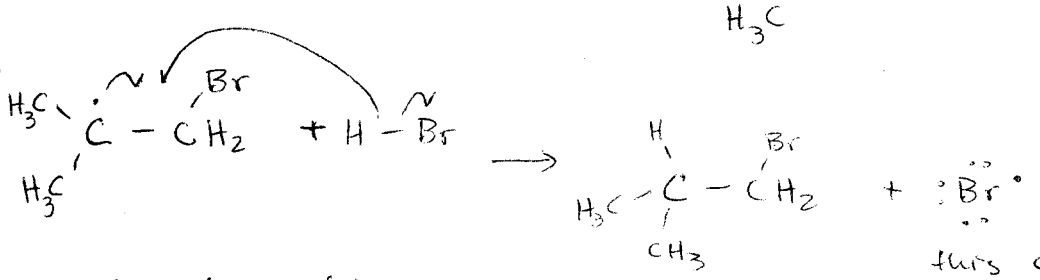
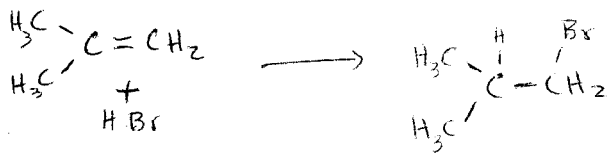
Chain Propagation

(1) 

(2) 

Overall, for (1) + (2)



this goes on to react as in (1)

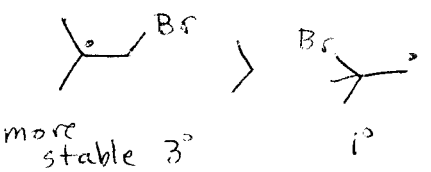
only HBr - not HCl, HF, etc! complicated ~~bs~~ reasons

Origin of regioselectivity?

⟹ Set in step 1

2 components - rationale

1. Steric consideration - Br is large, so prefers less conjested side of alkene
2. Radical stability - parallels carbocation stability (both electron-deficient)



more stable 3° > 1°