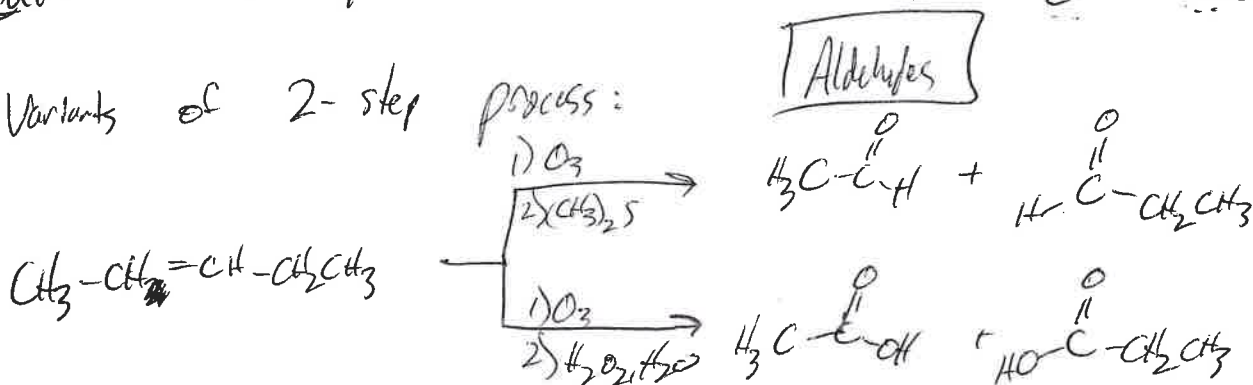


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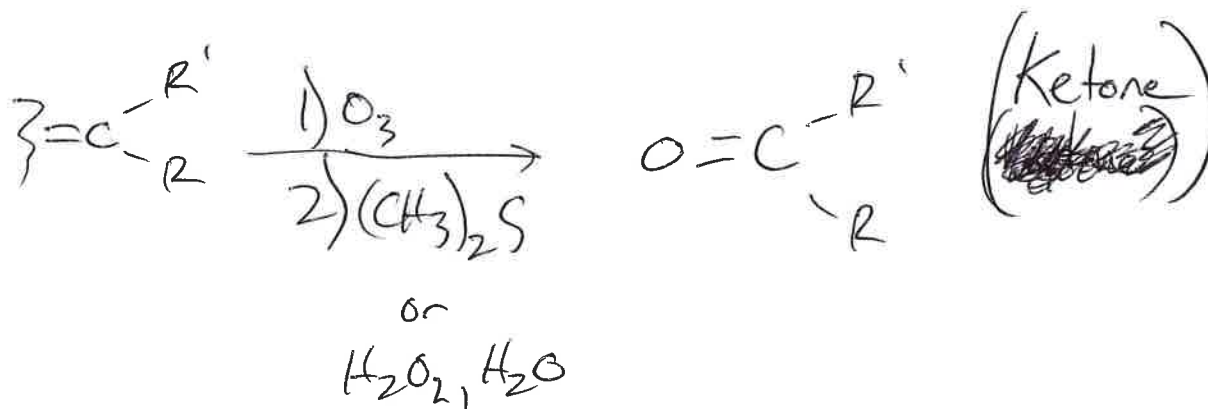
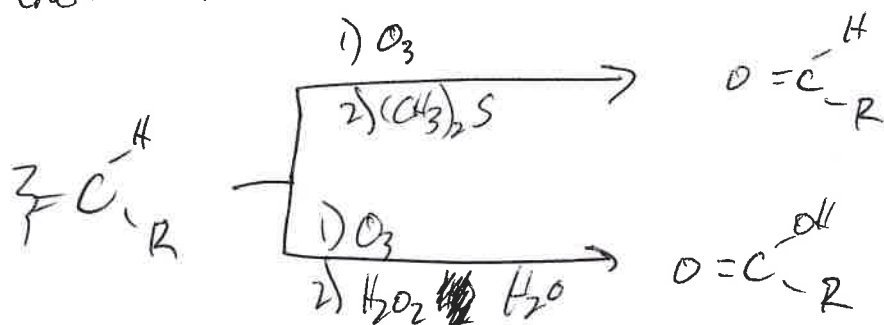
Recall: Ozonolysis of Alkenes



2 Variants of 2-step process:

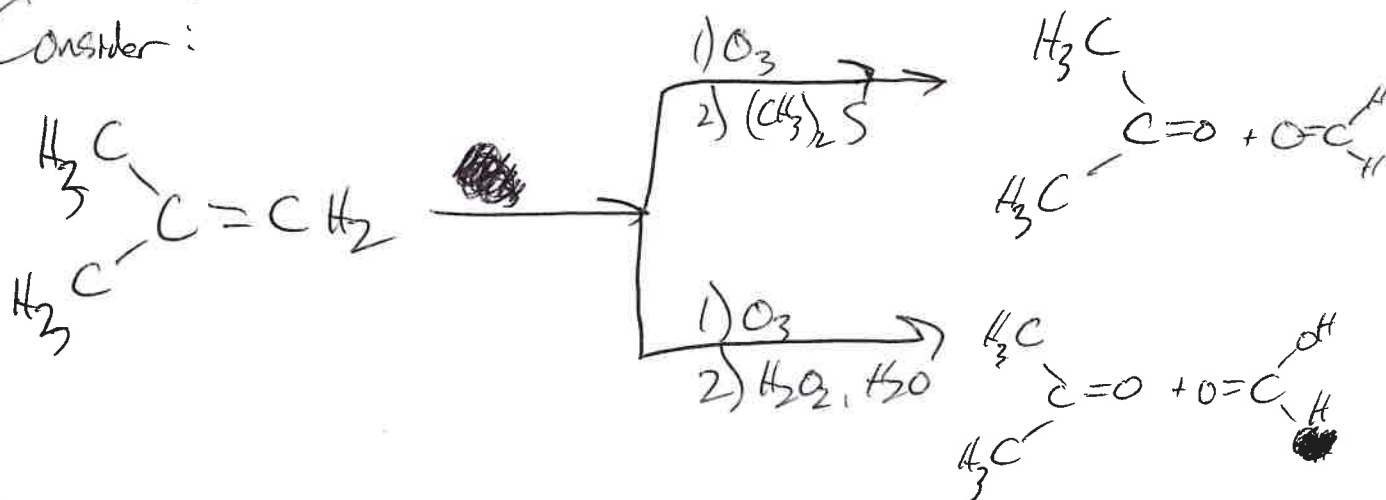


General Rules: (Table 5.1)

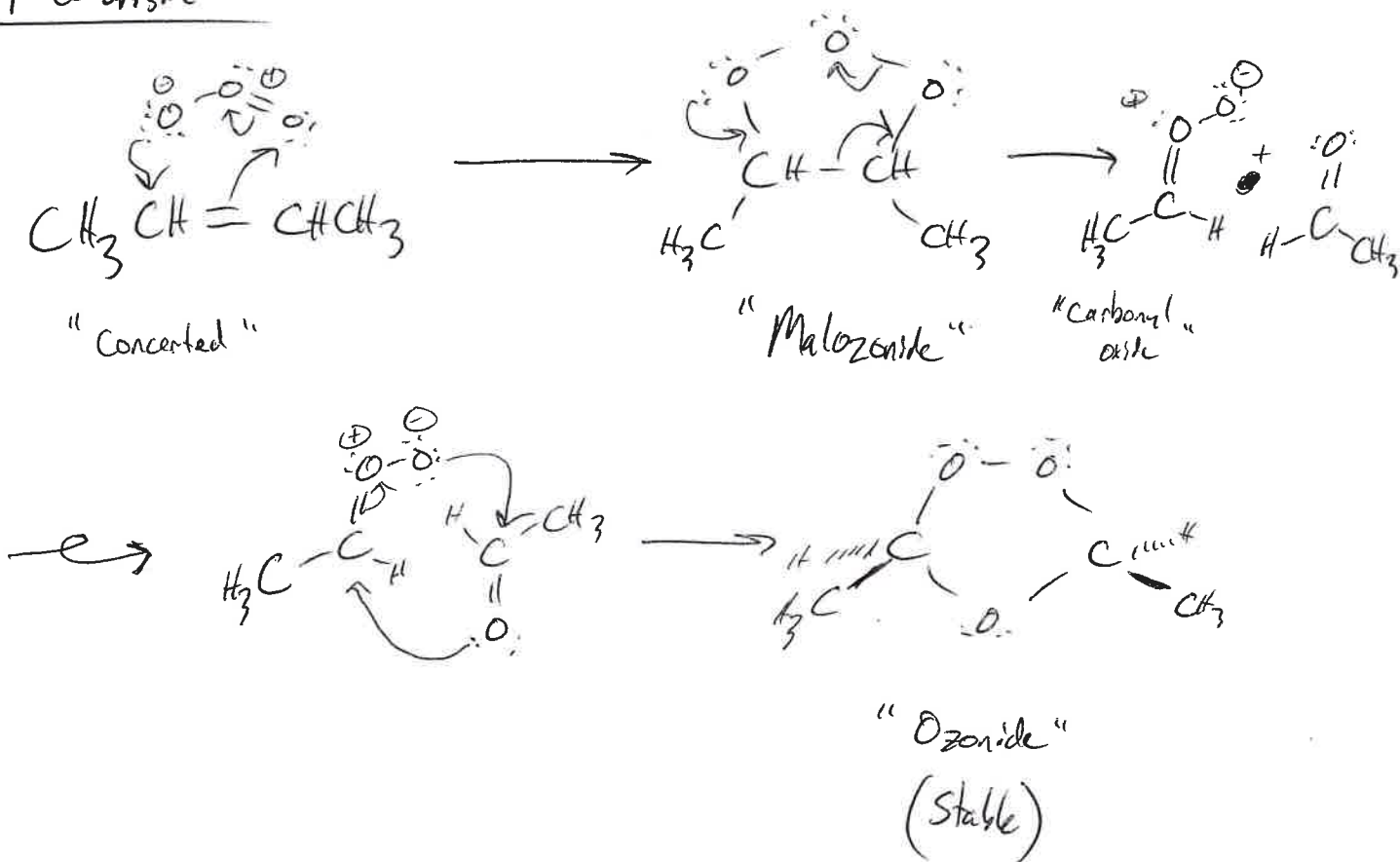


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Consider:



Mechanism

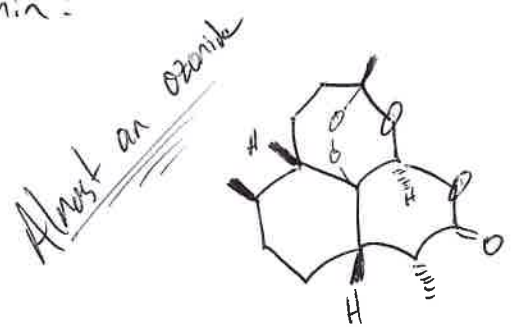


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Note: In ozonolysis, intermediate is the ozonide

Step 2:  $(CH_3)_2S$  vs.  $H_2O_2, H_2O \Rightarrow$  Mech. unclear

Artemisinin:



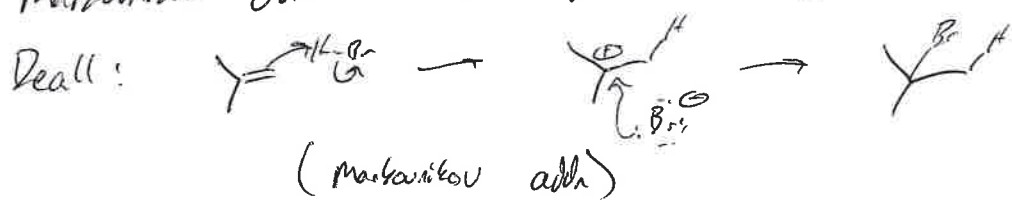
Dr. Youyou Tu

Anti-malarial agent

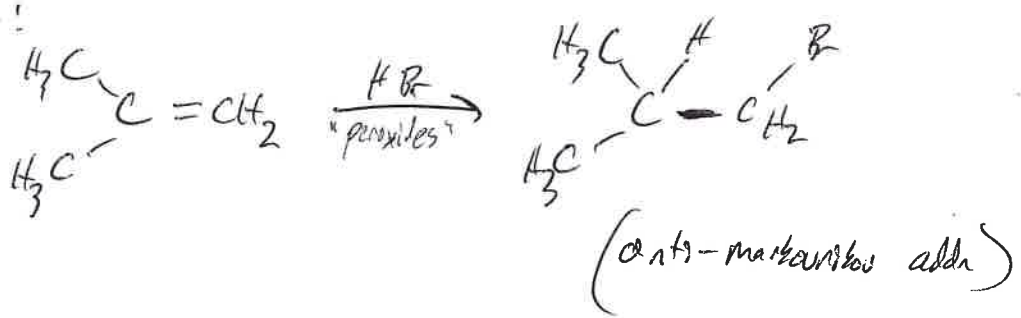
Synthetic ozonides as anti-malarial agents

\* See web site

Anti-Markovnikov addition of HBr (only) to alkenes



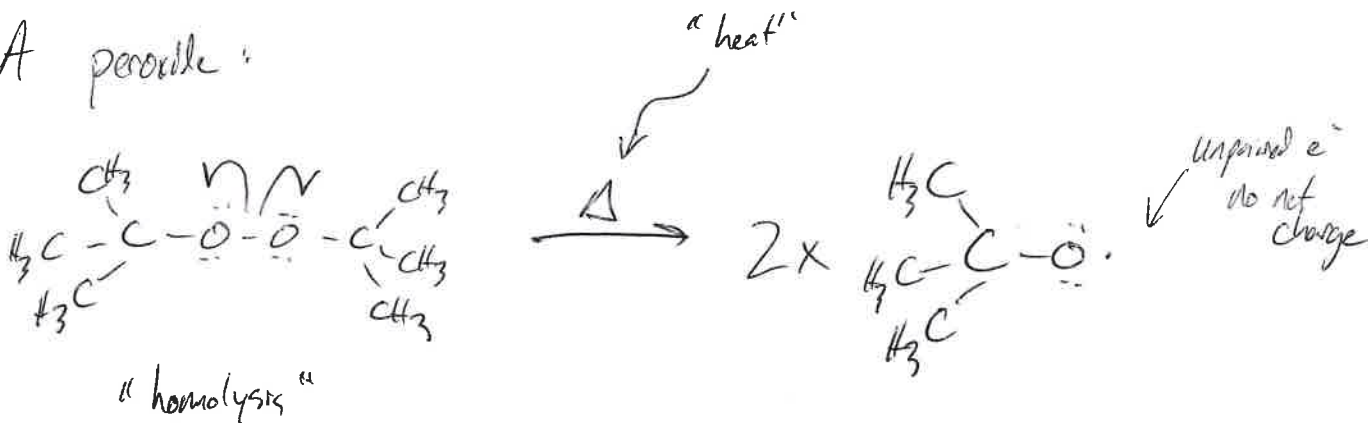
Contrast:



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This rxn involves radical intermediates (i.e., species with unpaired electrons) rather than ionic intermediates.

A peroxide:



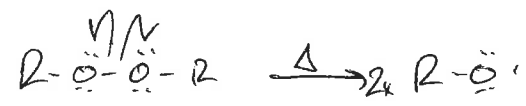
**Note:** bond breakage that occurs with both e<sup>-</sup>s is called heterolysis

$$\text{H}-\overset{\text{N}}{\text{R}}-\text{Br} \longrightarrow \text{H}^{\oplus} + \overset{\ominus}{\text{Br}}$$

"heterolysis"

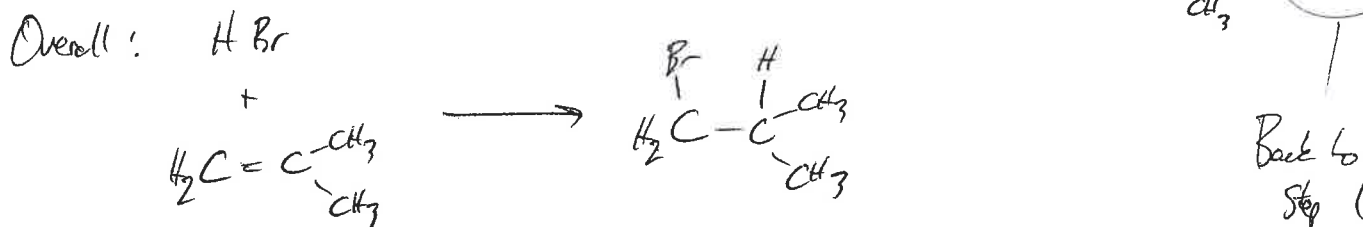
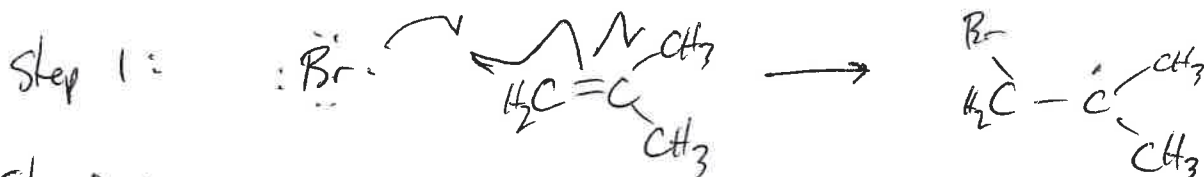
Mech Hypothesis ("chain reaction" mech)

Initiation (creates radical species)



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Propagation



Origin of Selectivity?

Carbon centered radicals are  $e^-$ -deficient.  
 $\rightarrow$  stability trends parallel carbocation trends

