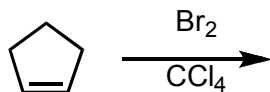
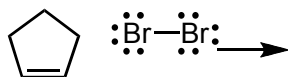


## 1 Di-bromination of Alkenes

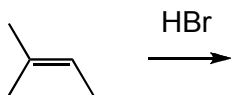
Example

- the reaction is **STEREOSPECIFIC**, the trans-product is formed in preference to the cis-product
- $\text{CCl}_4$  - carbon tetrachloride - inert nonpolar solvent (doesn't get involved in the reaction)
- need to explain this product distribution - need a **MECHANISM!**

Mechanism

- **ANTI** addition, bromines add to **opposite** sides of the  $\text{C}=\text{C}$  double bond (top and bottom)
- note new type of structure for indicating stereochemistry on rings, trans- in this case
- **NOTE**, because of bromonium ion intermediate (no "free" carbocation) there are no rearrangements - we will use this information later!

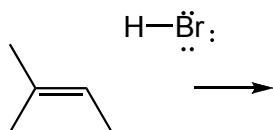
## 2 Mono-bromination of Alkenes



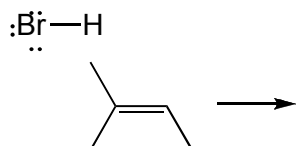
- the reaction is **REGIOSPECIFIC** since **ONE** the position of the Br is favored over the other

Question: how do we explain this product distribution, i.e. the regioselectivity?

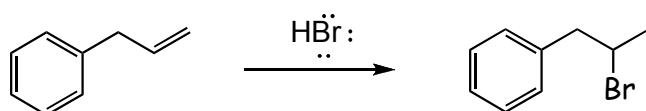
Answer: look at the mechanism!



compared to.....

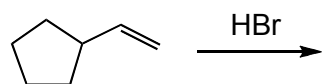


Markovnikov Rule: Electrophilic addition proceeds via the most stable intermediate. The Markovnikov product is that expected by electrophilic addition via the most stable intermediate

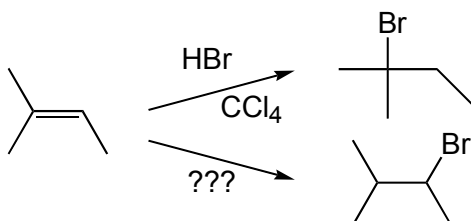


- a "hydride shift" occurred to form a more stable cation intermediate
- the hydrogen atom moved with BOTH electrons, i.e. equivalent to a hydride anion
- cations are PRONE to such rearrangements
- in our courses, **ALWAYS** rearrange a carbocation intermediate to a more stable one **if possible!**

#### Example Problem



#### Anti-Markovnikov?



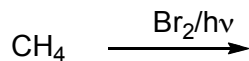
- Anti-Markovnikov is possible, but it requires a Radical mechanism

## 2 Radical Mechanisms

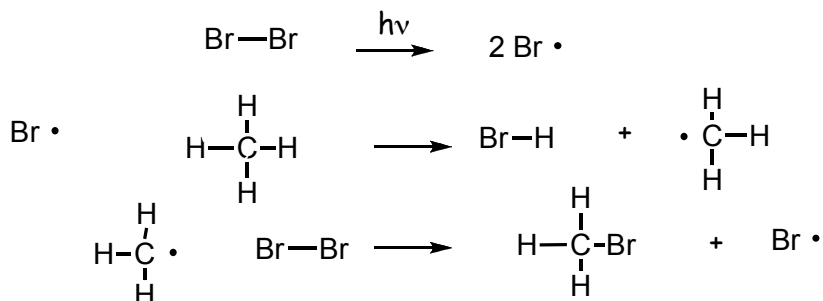
- Most reactions occur via 2-electron mechanisms (e.g. H-Br + alkene)
- Radical reactions usually occur via 1-electron mechanisms that involve **HOMOLYTIC CLEAVAGE**

Example: photobromination of methane  $h\nu = \text{light (energy)}$

**the reaction**

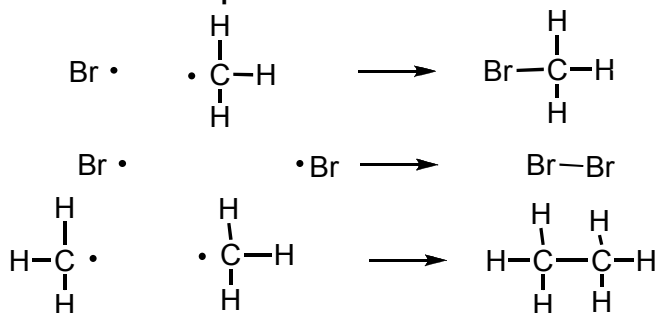


**the mechanism**

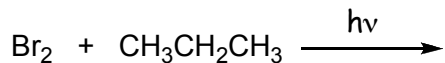


- Note, all bond cleavage processes are HOMOLYTIC, and are described in terms of bond dissociation energies

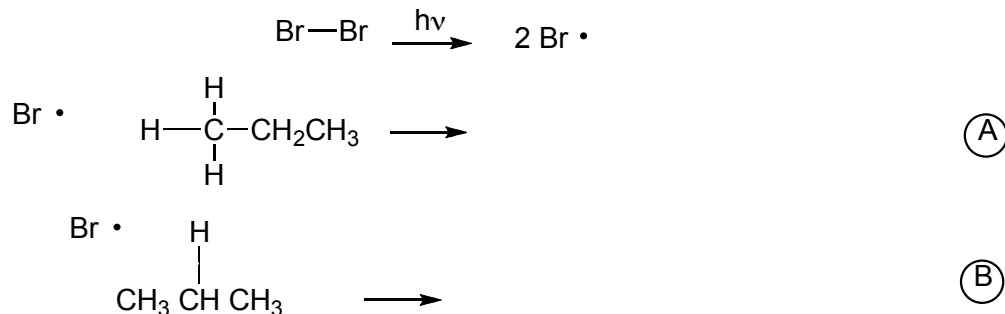
**common termination steps**



Photobromination of propane



**partial mechanism** to account for this observation



**each process** makes an H-Br bond and breaks a C-H bond:

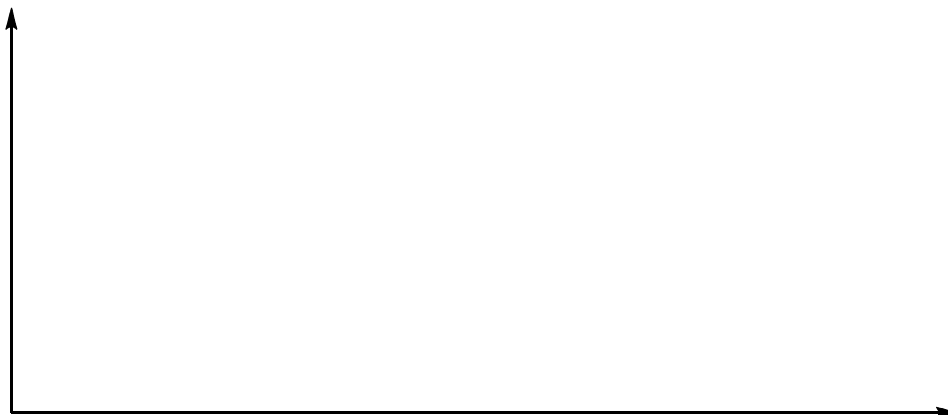
compare the energy requirements of the critical radical formation steps (A and B above)

1°  $\Delta H = 98$  (1° carbon) - 88, i.e. abstraction by Br• endothermic by 10 kcal/mol

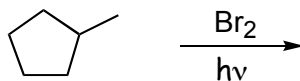
2°  $\Delta H = 95$  (2° carbon) - 88, i.e. abstraction by Br• endothermic by 7 kcal/mol

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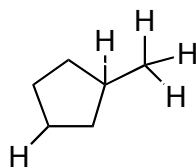
• Hammond postulate predicts a larger difference in activation energies, larger difference in rates, increased selectivity for two ENDOTHERMIC REACTIONS such as these



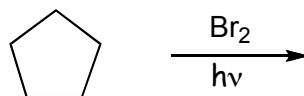
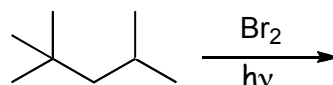
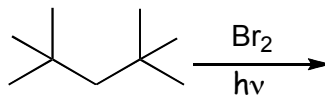
Example Reactions



Different types of H could have been abstracted by the Br•

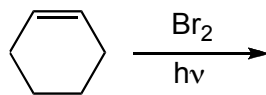


Example problems: give the major organic products of the following reactions



- EACH reaction proceeds via the most stable radical intermediate (shown in parenthesis), since that is the intermediate that will be formed FASTEST
- note however, that in practice this reaction is only really useful if there is an obvious radical site that is more stable than any others, otherwise there will be multiple products

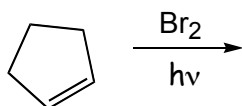
### Allylic Bromination



### Mechanism

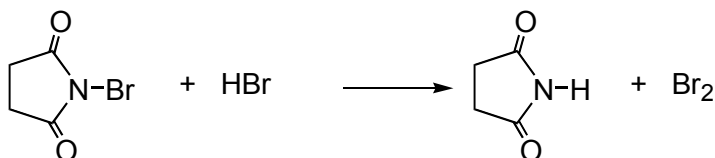
- This is the SAME mechanism as before, this time the radical is resonance stabilized

Wait a minute, didn't we just learn that Br<sub>2</sub> ADDS to C=C bonds?

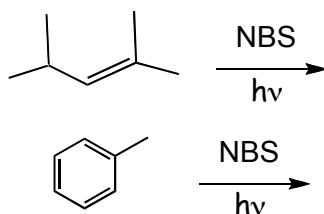


Solution: use a very low concentration of Br<sub>2</sub> to minimize direct reaction with the alkene

### New reagent

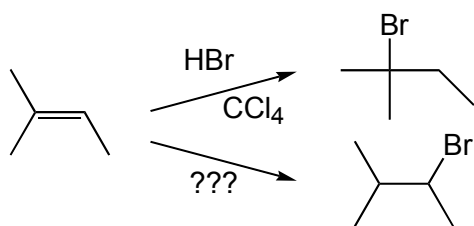


### Examples

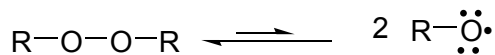


- Bottom line, use NBS/hv as the reagents for allylic bromination, not Br<sub>2</sub>/hv
- Can use EITHER Br<sub>2</sub>/hv OR NBS/hv to brominate alkanes, so....
- Just use NBS/hv to brominate EVERYTHING so that you don't have to remember which reagent to use when

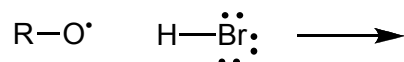
## 4.7 Radical Addition: Anti-Markovnikov Addition of HBr



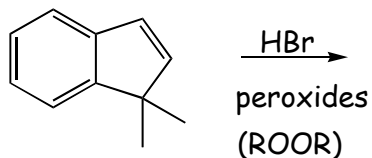
New reagent



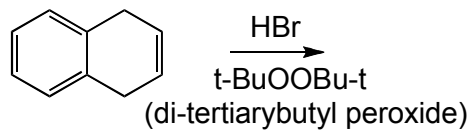
Mechanism



Example



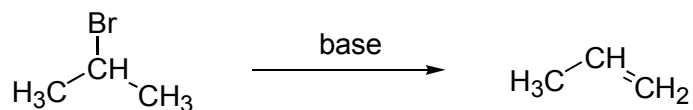
- the reaction is REGIOSPECIFIC, the -Br adds to the LEAST substituted "end" of the C=C bond



## 2 Synthesis of Alkenes

### 2.1 From Alkyl Halides (seen before, review)

- i.e. reactions of alkyl halides that have alkenes as the **products**
- in useful reactions we want avoid carbocations, thus we want to do E2 elimination



Which base to use to ensure elimination versus S<sub>N</sub>2???? Remember.....

- E2 reaction is favored for 3° halides
- For 2° halides, E2 can be forced over S<sub>N</sub>2 by using a bulky base, see below
- For 3° halides, a bulky base is not necessary, the product will be the Saytzeff product
- For 3° halides, a bulky base will give the least substituted alkene, for steric reasons

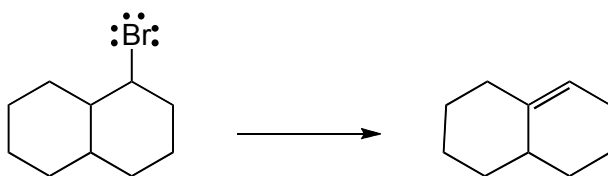
Examples of bulky bases

diisopropylamine (i-Pr<sub>2</sub>NH)

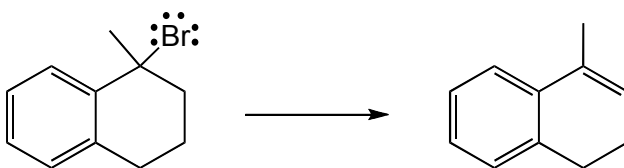
t-butoxide (t-BuO<sup>-</sup>)

dimethylpyridine

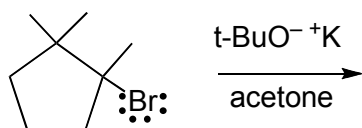
Example Reactions



- 2° halide, use bulky base to ensure no S<sub>N</sub>2, get Saytzeff alkene product



- 3° halide, use NON-bulky base (no S<sub>N</sub>2 not possible), get Saytzeff alkene product



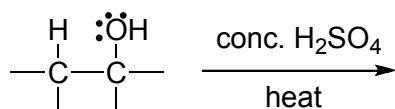
- 3° halide, use BULKY base and get Non-Saytzeff (Hoffmann) alkene product

Bottom line

- for 2° halides, use t-BuO<sup>-</sup> to ensure no S<sub>N</sub>2 and to obtain Saytzeff product
- for 3° halides, use CH<sub>3</sub>O<sup>-</sup> to obtain Saytzeff product and t-BuO<sup>-</sup> to obtain Hoffman product

## 2.2 From Alcohols (E1 and E2 elimination in a new context)

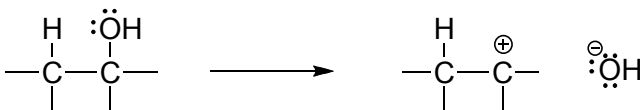
The reaction



- note a special kind of **SOLVENT EFFECT** here! In an aqueous medium, acid catalyzes water ADDITION to the alkene to make an alcohol. In conc. sulfuric acid medium, the acid helps to REMOVE water from an alcohol to make an alkene (the sulfuric acid DEHYDRATES the alcohol)

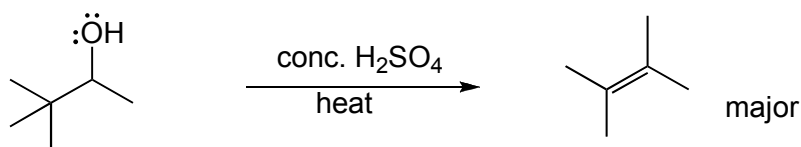
Mechanism: you already know it - either an E1 or an E2 elimination!

• in the mechanism, H<sub>2</sub>O is the leaving group, <sup>-</sup>OH is a poor leaving group (this is an important general principle that we will return to again later....)



• in general, small neutral molecules such as water make excellent leaving groups, since they tend to contain low energy electrons

Example



- 3° and 2° alcohols almost certainly E1 mechanism
- carbocation intermediates means rearrangements
- the sulfuric acid is the initial acid, the bisulfate anion is a likely base to deprotonate, recovering the acid catalyst



TEST YOURSELF. Provide the missing reagents/conditions or major organic products for the following reactions.

