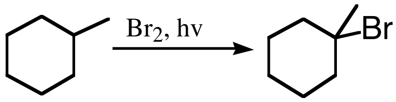
Chem 350 Jasperse Ch. 6 Summary of Reaction Types, Ch. 4-6, Test 2

1. Radical Halogenation (Ch. 4)



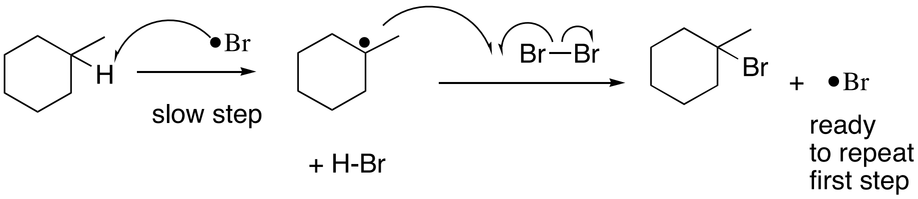
resonance stabilized>3°>2°>1°>alkenyl

Recognition: X_2, hv

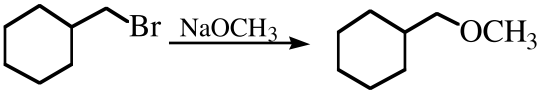
Predicting product: Identify which carbon could give the most stable radical, and substitute a Br for an H on that carbon.

Stereochemistry: Leads to racemic, due to achiral radical intermediate.

Mech: Radical. Be able to draw propagation steps.



2. S_N2 Substitution



S_N2: 1°>2°>3°> alkenyl

Any of a large variety of nuclophiles or electrophiles can work.

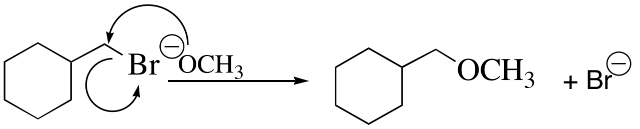
Recognition: A. Anionic Nucleophile, and
B. 1° or 2° alkyl halide

(3° alkyl halides fail, will give E2 upon treatment with Anionic Nucleophile/Base. For 2° alkyl halides, S_N2 is often accompanied by variable amounts of E2.)

Predicting product: Replace the halide with the anion nucleophile

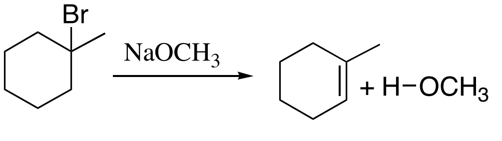
Stereochemistry: Leads to Inversion of Configuration

Mech: Be able to draw completely. Only one concerted step!



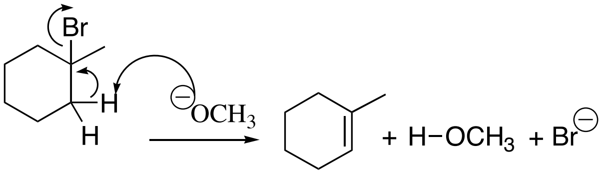
S_N2: 1°>2°>3°> alkenyl

3. E2 Reactions.



E2: 3°>2°>1°> alkenyl

Mech:



Recognition: A. Anionic Nucleophile/Base, and
B. 3° or 2° alkyl halide

(1° alkyl halides undergo S_N2 instead. For 2° alkyl halides, E2 is often accompanied by variable amounts of S_N2.)

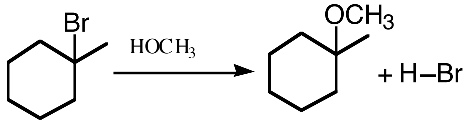
Orientation: The most substituted alkene forms (unless a bulky base is used, ch. 7)

Predicting product: Remove halide and a hydrogen from the neighboring carbon that can give the most highly substituted alkene. The hydrogen on the neighboring carbon must be trans, however.

Stereochemistry: Anti elimination. The hydrogen on the neighbor carbon must be trans/anti.

Mech: Concerted. Uses anion. Be able to draw completely. Only one concerted step!

4. S_N1 Reactions.



S_N1: resonance >3°>2°>1°> alkenyl

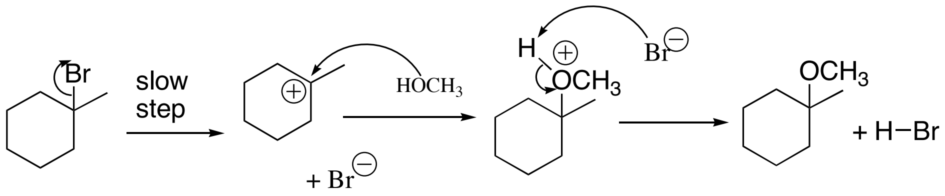
Recognition: A. Neutral, weak nucleophile. No anionic nucleophile/base, and
B. 3° or 2° alkyl halide. (Controlled by cation stability).

(1° alkyl halides undergo S_N2 instead. For 2° alkyl halides, S_N1 is often accompanied by variable amounts of E1.)

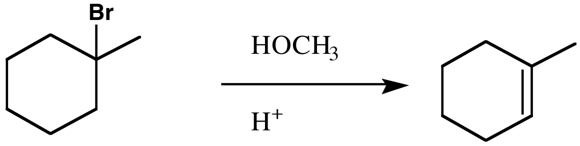
Predicting product: Remove halide and replace it with the nucleophile (minus an H atom!)

Stereochemistry: Racemization. The achiral cation intermediate forgets any stereochem.

Mech: Stepwise, 3 steps, via carbocation. Be able to draw completely.



5. E1 Reactions. 3° > 2° > 1° (Controlled by cation stability)



E1: 3°>2°>1

Recognition: A. Neutral, weak nucleophile. No anionic nucleophile/base, and
B. 3° or 2° alkyl halide. (Controlled by cation stability).

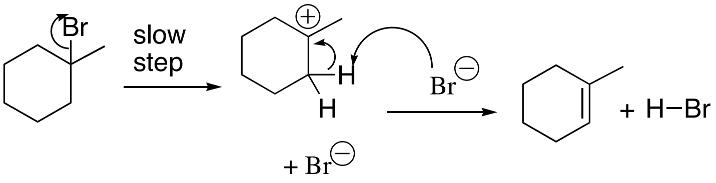
(For 2° alkyl halides, E1 is often accompanied by variable amounts of S_N1.)

Orientation: The most substituted alkene forms

Predicting the major product: Remove halide and a hydrogen from the neighboring carbon that can give the most highly substituted alkene. The hydrogen on the neighboring carbon can be cis or trans.

Stereochemistry: Not an issue. The eliminating hydrogen can be cis or trans. .

Mech: Stepwise, 2 steps, via carbocation. Be able to draw completely.



Sorting among S_N2, S_N1, E2, E1: How do I predict?

Step 1: **Check nucleophile/base**.

- If **neutral**, then **S_N1/E1** → mixture of both
- If **anionic**, then **S_N2/E2.**

Step 2: If **anionic**, and in the **S_N2/E2**, then **Check the substrate**.

  - 1° → **S_N2**
  - 2° → **S_N2/E2 mixture.** Often more **S_N2**, but not reliable…
  - 3° → **E2**