Alkene Addition Reactions: Complete Study Guide

This guide covers the five foundational addition reactions of alkenes: hydrohalogenation, halogenation, acid-catalyzed hydration, oxymercuration-demercuration, and hydroboration-oxidation. Each section breaks down the mechanism step by step, explains regiochemistry and stereochemistry, and highlights the most commonly tested exam concepts. For alkene structure, naming, and bonding fundamentals, see the companion guide: Alkenes: Structure, Naming, and Reactivity. Drawing on Clayden, Wade, McMurry, Chemistry LibreTexts, Master Organic Chemistry, and primary literature.

Reaction	Reagent	Product	Regiochem.	Stereochem.	Rearrange?
Hydrohalogenation	HX	Alkyl halide	Markovnikov	Racemization	Yes
Halogenation	Br_2 / Cl_2	Vicinal dihalide	Anti-Markov. (X)*	Anti	No
Acid Hydration	H_2O / H_2SO_4	Alcohol	Markovnikov	Racemization	Yes
Oxymercuration	$Hg(OAc)_2/H_2O$; $NaBH_4$	Alcohol	Markovnikov	Racemization #	No
Hydroboration-Ox.	BH_3; H_2O_2/NaOH	Alcohol	Anti-Markovnikov	Syn	No

*Markovnikov OH regiochemistry applies in halohydrin formation when water acts as nucleophile.

due to NaBH4, the anti-stereochemistry of the original step is scrambled and therefore creates a mixture of stereochemistries.

As you go through the study guide, please read carefully to understand these mechanisms and fundamentals!

Part 1: Hydrohalogenation of Alkenes (HX Addition)

Hydrohalogenation is an electrophilic addition reaction in which a hydrogen halide (HX) adds across the double bond to form an alkyl halide. It is the entry point to carbocation chemistry and Markovnikov's rule.

- Reaction type: Electrophilic addition (two-step)
- Reagent: HCl, HBr, or HI (reactivity order: HI > HBr > HCl)
- Product: Alkyl halide
- Regiochemistry: Markovnikov — X to more-substituted carbon
- Prone to carbocation rearrangements (hydride or alkyl shifts)

Mechanism

Step 1: Protonation of the Alkene (Rate-Determining Step)

The π electrons attack the electrophilic H of HX. A C–H bond forms at the less-substituted carbon; X^- departs; a carbocation forms at the more-substituted carbon. This is the slow, rate-limiting step.

Carbocation Type	Relative Stability
Tertiary (3°)	Most stable — stabilized by hyperconjugation from 3 alkyl groups
Secondary (2°)	Moderate stability
Primary (1°)	Unstable — avoid when possible
Methyl	Least stable

> Hyperconjugation: adjacent C–H and C–C σ-bonds donate electron density into the empty p-orbital of the carbocation. More substitution = more stabilization = lower activation energy for the rate-limiting step.

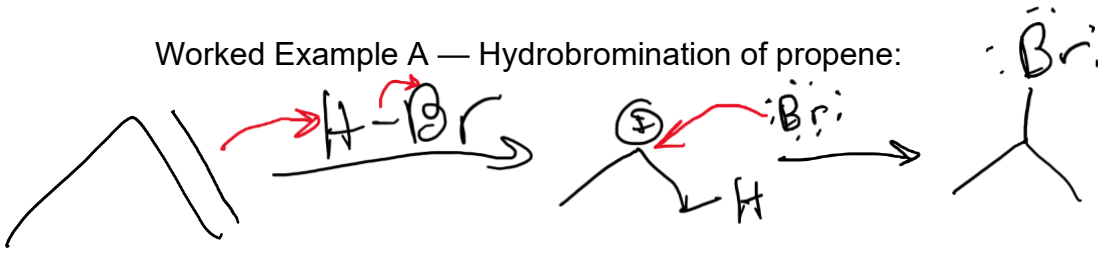
Step 2: Nucleophilic Attack by the Halide

X^- attacks the planar (sp^2) carbocation. Because the carbocation is flat, attack can occur from either face — if a new chiral center is created, a racemic mixture results.

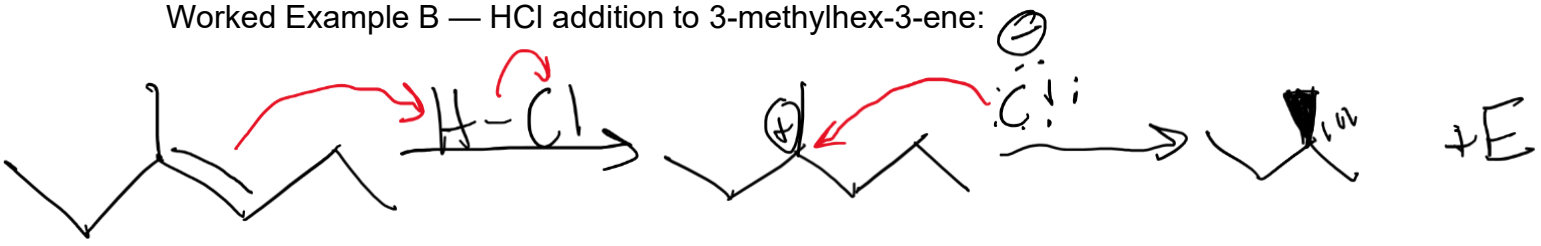
Markovnikov's Rule

> *H adds to the less-substituted carbon; X adds to the more-substituted carbon. The reaction proceeds through the most stable (most-substituted) carbocation intermediate.*

Worked Example A — Hydrobromination of propene:



Worked Example B — HCl addition to 3-methylhex-3-ene:



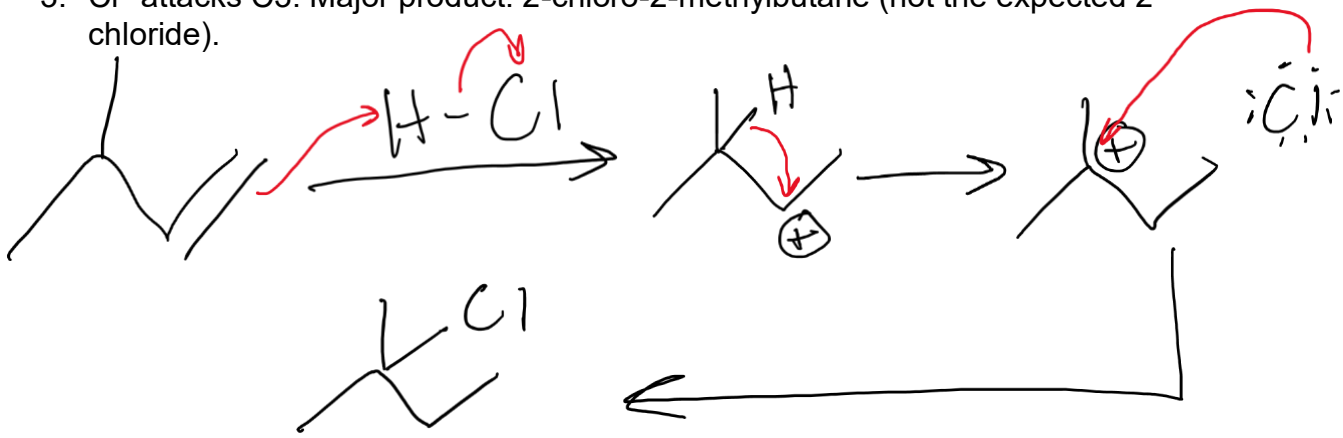
Carbocation Rearrangements

- Hydride shift (1,2-H shift): H migrates with its bonding electrons to an adjacent carbocation.
- Alkyl shift (1,2-alkyl shift): An entire alkyl group migrates, sometimes changing the carbon skeleton.

> Exam tip: Always check whether the initial carbocation can rearrange to give a more stable one. If yes, the rearranged product is the major product.

Worked Example C — HCl addition to 3-methyl-1-butene:

1. H^+ adds to C1; secondary (2°) carbocation at C2.
2. 1,2-hydride shift: H migrates from C3 to C2 → tertiary (3°) carbocation at C3.
3. Cl^- attacks C3. Major product: 2-chloro-2-methylbutane (not the expected 2° chloride).



Quick Recap — Hydrohalogenation

✓ Tertiary/secondary alkenes → stable carbocation, good yield

✓ HBr or HI → stronger acids, faster reaction

✗ Primary positions → unstable 1° carbocation

✗ HF → weakest HX acid; not used in simple addition

Part 2: Halogenation of Alkenes (X_2 Addition)

Treatment of an alkene with Br_2 or Cl_2 gives a vicinal dihalide via a cyclic halonium ion. This is the defining example of anti addition in alkene chemistry.

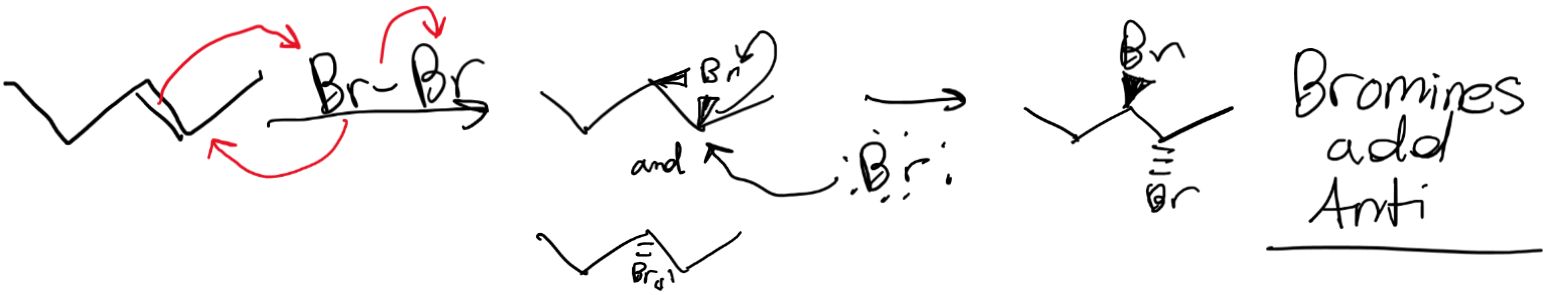
- Reaction type: Electrophilic addition (two-step, no acid required)
- Reagents: Br_2 or Cl_2 in CH_2Cl_2 or CCl_4 (F_2 too reactive; I_2 thermodynamically unfavorable)
- Product: Vicinal dihalide (or halohydrin if water present)
- Intermediate: Cyclic bromonium/chloronium ion — NOT a flat carbocation
- Stereochemistry: Anti addition exclusively
- Stereospecific: E and Z alkenes give different product stereoisomers

Mechanism

Step 1: Bromonium Ion Formation

The π electrons attack one Br of Br_2, polarizing the Br–Br bond. One Br bridges both alkene carbons simultaneously forming a strained three-membered cyclic ring — the bromonium ion — while Br^- departs as the leaving group.

> Critical: The bromonium ion is NOT a flat carbocation. Bromine bridges both carbons, completely blocking one face. This is why anti addition is mechanistically enforced — there are no exceptions.



Step 2: Backside Attack by Bromide

Br^- attacks one of the two electrophilic carbons from the backside (opposite the bridging Br) — directly analogous to SN2 inversion. Both halogens end up on opposite faces: anti addition.

Worked Example A — Br_2 addition to cyclopentene:

1. Bromonium ion forms (from either face equally).
2. Br^- attacks from the opposite face.
3. Product: exclusively trans-1,2-dibromocyclopentane. Cis isomer NEVER forms.

Exam trap: Never predict a cis product from X_2 addition. The bromonium mechanism makes syn addition mechanistically impossible.

Stereospecificity: E vs Z Alkenes

Starting Alkene	Product after Anti Addition
(E)-2-butene (trans)	Meso compound: (2R,3S)-2,3-dibromobutane only
(Z)-2-butene (cis)	Racemic mixture: (2R,3R) + (2S,3S) dibromobutane (50:50)

Halohydrin Formation (X_2 + H_2O)

When Br_2 is added in water as solvent, water (in vast excess) attacks the bromonium ion preferentially as the nucleophile. OH installs on the more-substituted carbon (Markovnikov-like); Br installs on the less-substituted carbon. Stereochemistry is still anti.

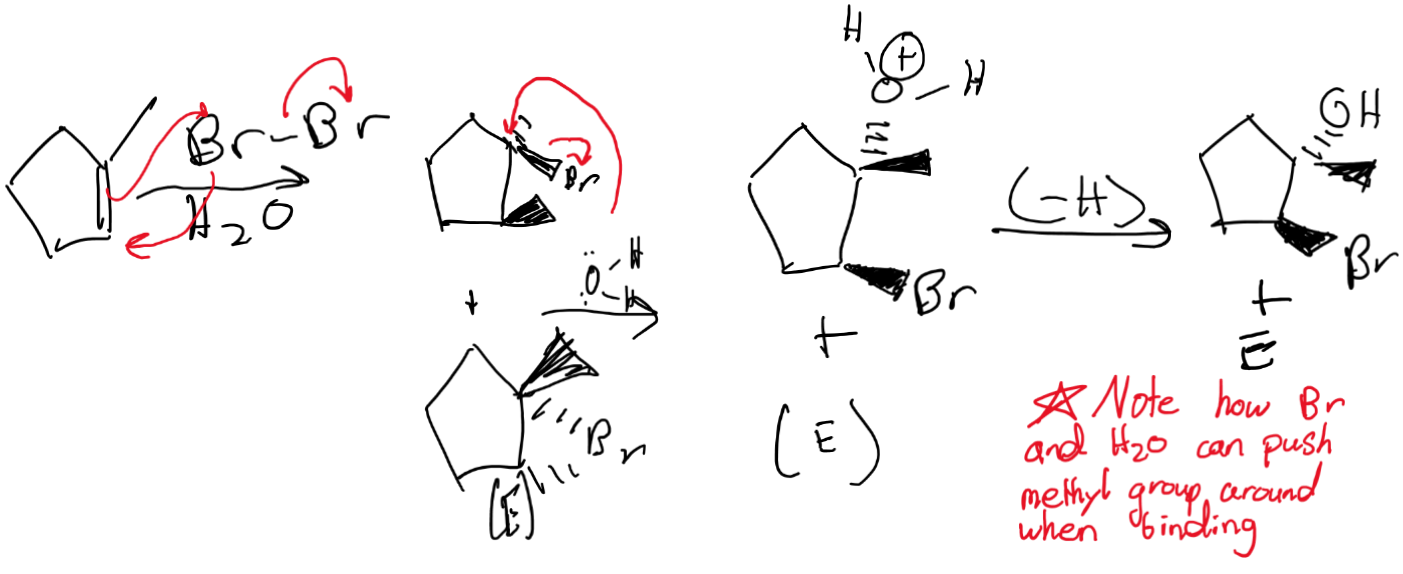
In halohydrin formation: OH → more-substituted carbon. Br → less-substituted carbon. Stereochemistry → anti. No carbocation intermediate — no rearrangements.

Bromine Test for Unsaturation

Alkene + Br_2 (orange/red) → vicinal dibromide (colorless). Immediate decolorization indicates a C=C double bond.

Quick Recap — Halogenation

- ✓ Br_2 or Cl_2 + alkene → vicinal dihalide (anti addition)
- ✓ Br_2/H_2O + alkene → bromohydrin (anti; Markovnikov OH)
- ✓ E alkene → meso product; Z alkene → racemic mixture
- ✗ F_2 → too reactive; I_2 → thermodynamically unfavorable
- ✗ Syn addition impossible via bromonium ion mechanism



Part 3: Acid-Catalyzed Hydration of Alkenes

Acid-catalyzed hydration adds water across the double bond using H_2SO_4 as catalyst to give the Markovnikov alcohol. It is the reverse of acid-catalyzed dehydration and illustrates equilibrium thinking alongside carbocation mechanism.

- Reaction type: Electrophilic addition (3-step), reversible
- Reagents: H_2O (excess) + dilute H_2SO_4 (acts as H_3O^+)
- Product: Alcohol (OH to more-substituted carbon)
- Regiochemistry: Markovnikov
- Stereochemistry: Racemization at any new chiral center (planar carbocation)
- Prone to carbocation rearrangements
- Acid is a true catalyst — consumed in Step 1, regenerated in Step 3

Why Acid is Required

Water (pKa 15.7) is far too weak to protonate a π bond on its own. Hydronium ion (H_3O^+) in strong acid solution is the actual proton source. Because H_3O^+ is consumed in Step 1 and regenerated in Step 3, it is a true catalyst.

> Use dilute H_2SO_4, not HCl. Bisulfate (HSO_4^-) is a weak nucleophile and will not compete with water for the carbocation. HCl gives a mixture of hydrohalogenation and hydration products.

Three-Step Mechanism

Step 1: Protonation of the Alkene (Rate-Determining Step)

H_3O^+ protonates the π bond, placing H on the less-substituted carbon and generating the most stable carbocation at the more-substituted carbon. Slow step.

Step 2: Nucleophilic Attack by Water

Water attacks the planar sp^2 carbocation with a lone pair, forming an oxonium ion ($R–OH_2^+$). Either face can be attacked → racemic mixture at any new chiral center. Fast step.

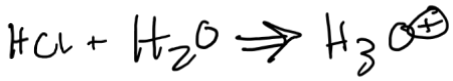
Step 3: Deprotonation (Catalyst Regenerated)

A second water molecule deprotonates the oxonium ion, regenerating H_3O^+ and yielding the neutral alcohol. Fast step.

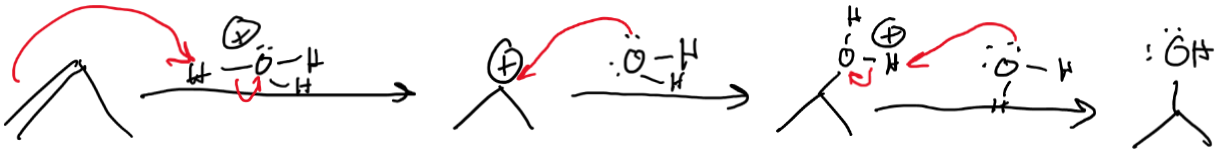
> *Net: alkene + H_2O → alcohol. H^+ consumed in Step 1, regenerated in Step 3 — it is a catalyst.*

Regiochemistry and Rearrangements

Worked Example A — Hydration of propene:



1. H_3O^+ protonates C1; secondary carbocation at C2.
2. H_2O attacks C2 → oxonium ion.
3. Deprotonation → 2-propanol (Markovnikov product).



Worked Example B — Hydration of 3-methyl-1-butene (rearrangement occurs):

1. H^+ adds to C1; 2° carbocation at C2.
2. 1,2-hydride shift: tertiary carbocation forms at C3.
3. H_2O attacks C3; deprotonation → 2-methyl-2-butanol (major product, NOT the expected 2° alcohol).

> Always check for rearrangements after the carbocation forms. The rearranged tertiary alcohol is often the actual major product.

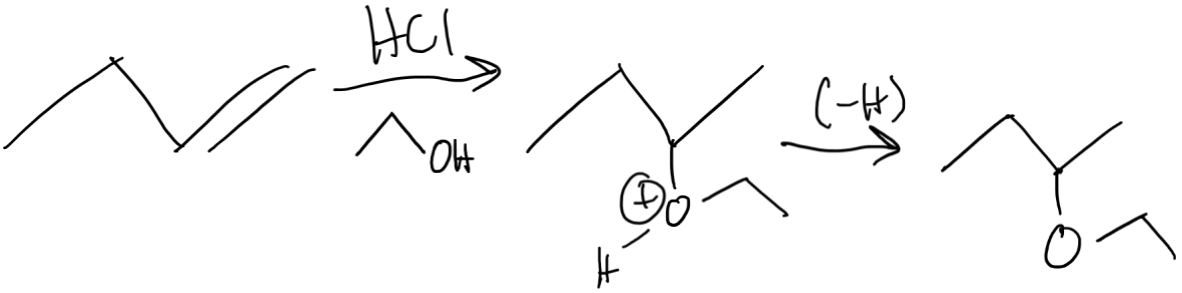
Equilibrium: Hydration vs Dehydration

Desired Product	Conditions to Favor (Le Chatelier)
Alcohol (hydration)	Excess water, lower temperature, dilute acid
Alkene (dehydration)	Concentrated acid, high temperature, remove water

Quick Recap — Acid-Catalyzed Hydration

- ✓ Tertiary/secondary alkenes → stable carbocation, good yield
- ✓ Dilute H_2SO_4 + excess H_2O → conditions that favor alcohol
- ✓ Use when Markovnikov alcohol is needed and rearrangement is not a concern
- ✗ Primary alkenes → unstable 1° carbocation, prone to rearrangement
- ✗ Need anti-Markovnikov alcohol? → use hydroboration-oxidation instead
- ✗ Need Markovnikov alcohol without rearrangement? → use oxymercuration instead

Note: H_2O can be replaced with alcohol to create ether



Part 4: Oxymercuration-Demercuration

Oxymercuration-demercuration is a two-step method for the Markovnikov hydration of alkenes that avoids the major drawback of acid-catalyzed hydration: carbocation rearrangements. It is the go-to method when a clean, predictable Markovnikov alcohol is needed from a substrate prone to rearrangement.

- Reaction type: Electrophilic addition via mercurinium ion (two steps total)
- Step 1 reagents: $Hg(OAc)_2$ / H_2O
- Step 2 reagent: $NaBH_4$ (reducing agent; replaces Hg with H)
- Product: Alcohol (Markovnikov — OH to more-substituted carbon)
- Stereochemistry: Anti addition through mercurinium ion; $NaBH_4$ step gives mixture at C–H
- No carbocation rearrangements — most important advantage over acid hydration
- No strong acid required — milder conditions

Mechanism

Step 1a: Mercurinium Ion Formation

Mercury in $Hg(OAc)_2$ carries a δ+ charge and is the electrophile. The π electrons of the alkene attack Hg, which simultaneously bonds to both alkene carbons forming a three-membered cyclic mercurinium ion — directly analogous to the bromonium ion — while acetate (OAc^-) departs.

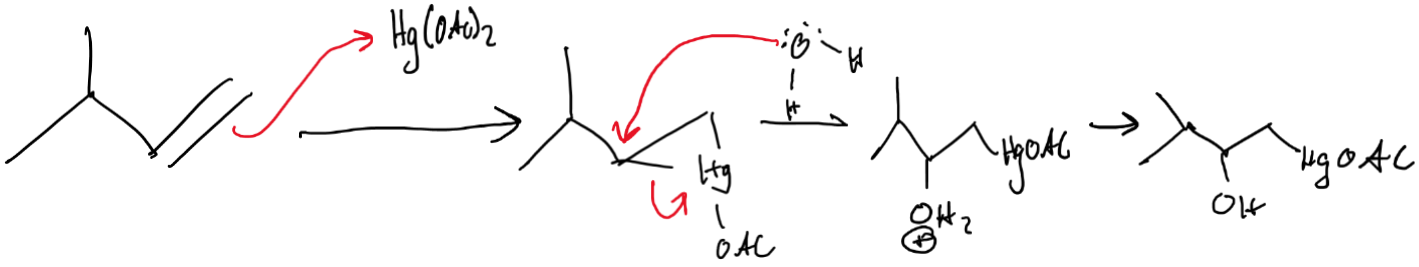
> Key: Because most of the positive charge in the mercurinium ion resides on mercury (not on carbon), the carbons never develop enough cationic character to trigger hydride or alkyl shifts. This is why rearrangements do not occur.

Step 1b: Nucleophilic Attack by Water

Water attacks the more-substituted (more electrophilic) carbon of the mercurinium ion from the backside (anti addition), installing –OH on the more-substituted carbon. Deprotonation gives an organomercury alcohol intermediate.

Worked Example A — Oxymercuration of 2-methylbut-2-ene (rearrangement-prone substrate):

1. Mercurinium ion forms; the tertiary carbon is more electrophilic.
2. H_2O attacks the tertiary carbon from the backside (anti).
3. Deprotonation of oxonium → organomercury alcohol intermediate.



This is where oxymercuration shines: a substrate that would rearrange under acidic conditions gives a clean, predictable product because no discrete carbocation ever forms.

Step 2: Demercuration ($NaBH_4$ Reduction)

$NaBH_4$ reduces the C–Hg bond, replacing mercury with hydrogen. This step is not stereospecific at the C–H carbon. The net result is Markovnikov addition of H and OH across the double bond, with no rearrangements.

Net: alkene + H_2O → Markovnikov alcohol. No rearrangements. No strong acid. Cleaner than acid-catalyzed hydration.

Oxymercuration vs Acid-Catalyzed Hydration

Feature	Acid Hydration vs Oxymercuration-Demercuration
Regiochemistry	Both give Markovnikov — OH to more-substituted carbon
Intermediate	Acid hydration: discrete carbocation | Oxymercuration: mercurinium ion
Rearrangements?	Acid hydration: YES | Oxymercuration: NO
Conditions	Acid hydration: strong acid | Oxymercuration: mild, $Hg(OAc)_2$
Reversibility	Acid hydration: reversible | Oxymercuration: irreversible
Overall stereochem.	Both: mixture at new chiral center (not stereospecific overall)

When to Choose Oxymercuration

- Substrate is prone to carbocation rearrangements (cyclopentyl, neopentyl-type substrates).
- A clean, predictable Markovnikov alcohol is needed in good yield.
- Harsh acidic conditions must be avoided (acid-sensitive groups elsewhere in the molecule).

Toxicity: Organomercury compounds are highly toxic. Mercury reagents require proper handling and disposal. Dimethylmercury has been responsible for laboratory fatalities. Always follow institutional safety protocols.

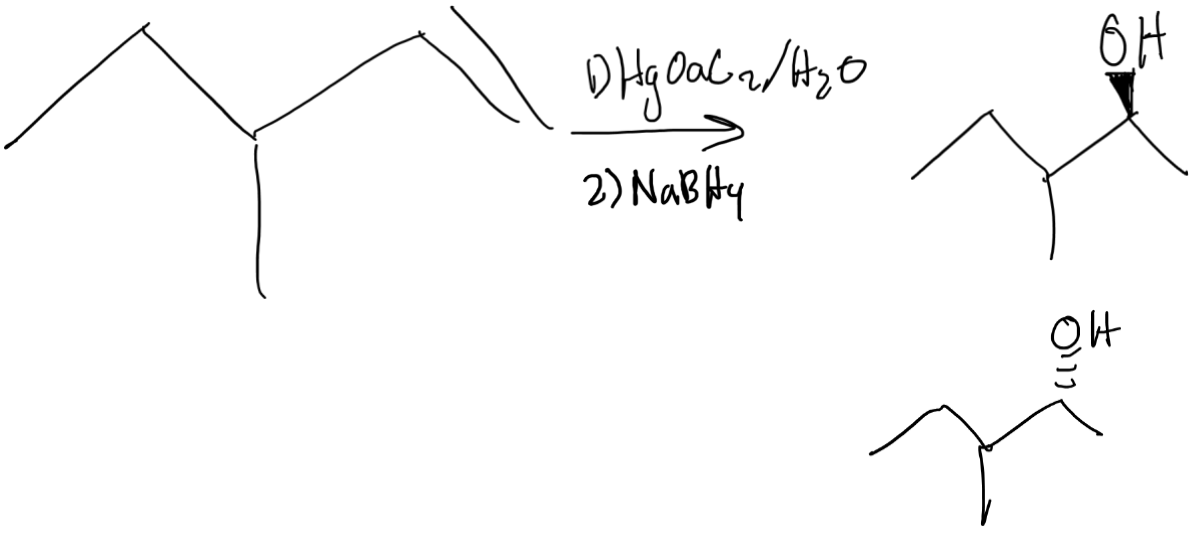
Ether Synthesis: Alkoxymercuration

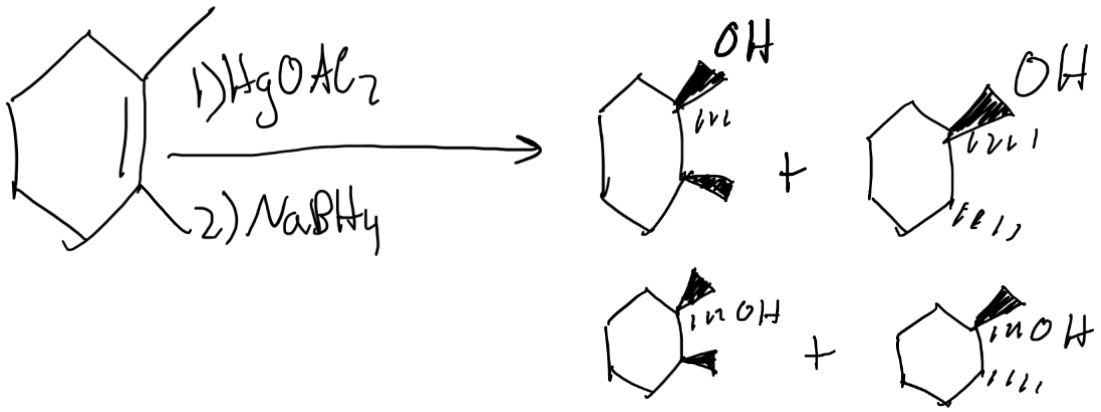
A useful variant: replace water with an alcohol (ROH) as solvent. The alcohol acts as the nucleophile in Step 1b, installing –OR on the more-substituted carbon. $NaBH_4$ reduction gives the Markovnikov ether product — with no rearrangements. This is called alkoxymercuration-demercuration.

Quick Recap — Oxymercuration-Demercuration

- ✓ Markovnikov alcohol — OH to more-substituted carbon
- ✓ No carbocation rearrangements — most important advantage
- ✓ Mild conditions — no strong acid required
- ✓ Anti addition through mercurinium ion
- ✓ Ether synthesis via alkoxymercuration (use ROH instead of H_2O)
- ✗ Not fully stereospecific overall ($NaBH_4$ step gives mixture at C–H)
- ✗ Organomercury compounds are toxic — careful handling required
- ✗ Anti-Markovnikov alcohol needed? → use hydroboration-oxidation

Examples





Part 5: Hydroboration-Oxidation of Alkenes

Hydroboration-oxidation, developed by Herbert C. Brown (Nobel Prize in Chemistry, 1979), is the premier method for anti-Markovnikov, syn-selective addition of water to an alkene. It is the direct synthetic complement to acid hydration and oxymercuration — those give the Markovnikov alcohol; hydroboration-oxidation gives the anti-Markovnikov alcohol.

- Reaction type: Concerted syn addition (Step 1), then oxidation (Step 2)
- Step 1 reagent: BH_3 (as BH_3·THF complex) or 9-BBN for enhanced steric selectivity
- Step 2 reagents: H_2O_2 / NaOH (hydrogen peroxide in basic solution)
- Product: Alcohol (anti-Markovnikov — OH to less-substituted carbon)
- Regiochemistry: Anti-Markovnikov
- Stereochemistry: Syn addition — H and OH add to the same face
- No carbocation intermediate — no rearrangements possible
- No acid required — mild conditions

Step 1: Hydroboration (Concerted, Syn Addition)

Boron in BH_3 has an empty p-orbital, making it a strong Lewis acid. The π electrons of the alkene interact with boron's empty orbital in a four-membered cyclic transition state in which B and H add simultaneously to the same face of the double bond. There is no intermediate — this is a concerted process.

Why Anti-Markovnikov?

Two factors drive boron to the less-substituted carbon:

1. Electronic: Boron is the electrophilic partner (δ+); H is the hydridic partner (δ−). Because there is no carbocation to stabilize, the electronic preference for placing a positive partial charge at the less-substituted carbon (which can better accommodate it) determines regiochemistry — the opposite of Markovnikov carbocation chemistry.
2. Steric: Boron's substituents are bulky enough that it preferentially bonds to the less hindered (less-substituted) carbon.

> Critical contrast: There is NO carbocation intermediate. B and H delivery occurs in one concerted step via a four-membered cyclic transition state. This enforces syn addition and makes rearrangements mechanistically impossible.

Because BH_3 adds across the alkene three times (giving a trialkylborane R_3B), all three additions are syn and anti-Markovnikov.

Step 2: Oxidation (H_2O_2 / NaOH)

Hydrogen peroxide in basic solution replaces the C–B bond with a C–O bond with complete retention of configuration at the carbon bearing boron. Because hydroboration was syn and oxidation proceeds with retention, the overall result is syn addition of H and OH across the double bond.

> *Net: alkene → anti-Markovnikov alcohol with syn stereochemistry. OH goes to less-substituted carbon; H goes to more-substituted carbon. Both add to the same face.*

Worked Examples

Worked Example A — Hydroboration-oxidation of 1-methylcyclopentene:

1. BH_3 adds B to C1 (less substituted) and H to C2, both to the same face (syn).
2. H_2O_2/NaOH: C–B → C–OH with retention. Product: trans-2-methylcyclopentanol (H and OH on the same face of the ring — cis relationship on the ring, anti-Markovnikov).

Worked Example B — Hydroboration-oxidation of propene:

1. B adds to C1 (terminal, less substituted); H adds to C2, syn.
2. Oxidation → 1-propanol (anti-Markovnikov).

> The synthetic power: acid-catalyzed hydration of propene gives 2-propanol (Markovnikov). Hydroboration-oxidation gives 1-propanol (anti-Markovnikov). Both regioisomers are now accessible from the same alkene.

Three-Way Comparison: Routes to Alkene Hydration

Feature	Acid Hydration / Oxymercuration	Hydroboration-Oxidation
Regiochemistry	Markovnikov (OH to more-sub)	Anti-Markovnikov (OH to less-sub)
Stereochemistry	Racemization / anti	Syn (stereospecific)
Intermediate	Carbocation or mercurinium ion	Concerted 4-membered cyclic TS
Rearrangements?	Acid hydration: yes | Oxymercuration: no	Never
Conditions	H_2SO_4/H_2O or $Hg(OAc)_2$	BH_3 then H_2O_2/NaOH; mild
Nobel Prize?	No	Yes — H. C. Brown, 1979

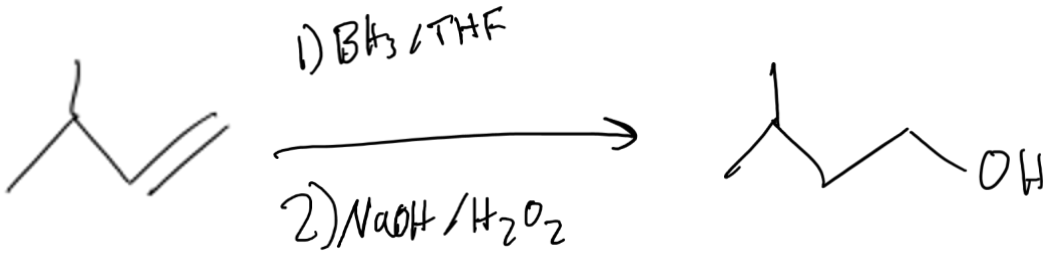
Quick Recap — Hydroboration-Oxidation

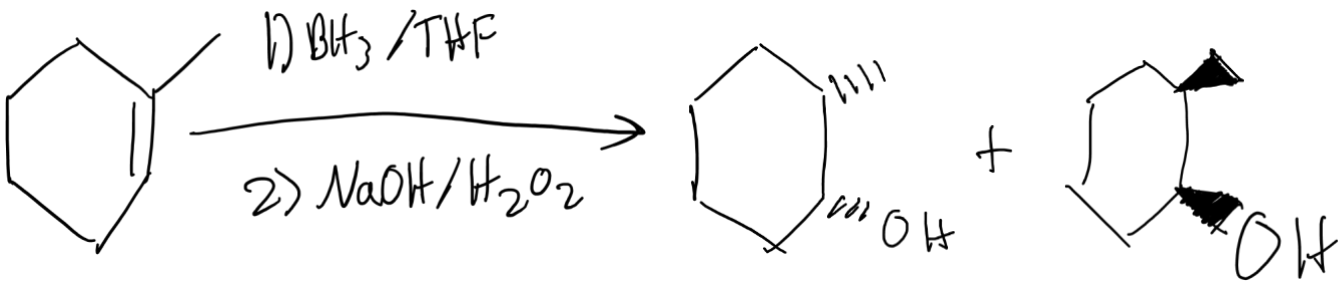
✓ Anti-Markovnikov alcohol — OH to less-substituted carbon

✓ Syn addition — H and OH add to the same face (stereospecific)

- ✓ No carbocation — no rearrangements ever
- ✓ Mild conditions — no acid, no heat required
- ✗ Markovnikov alcohol needed? → use acid hydration or oxymercuration
- ✗ BH_3 is reactive toward air and moisture — handle under inert atmosphere

Examples:





Note: OH and H add anti to one another, Hydrogen not drawn in.

Master Comparison: All Five Alkene Addition Reactions

Feature	Hydrohalog.	Halogenation	Acid Hydration	Oxymercuration	Hydroboration-Ox.
Steps	2	2	3	2 + $NaBH_4$	2 + H_2O_2/OH^-
Intermediate	Carbocation	Halonium ion	Carbocation + oxonium	Mercurinium ion	Cyclic 4-membered TS
Regiochem.	Markovnikov	Anti-Markov. (X)*	Markovnikov	Markovnikov	Anti-Markovnikov
Stereochem.	Racemization	Anti (stereospecific)	Racemization	Anti → then mixture	Syn (stereospecific)
Rearrangements?	Yes	No	Yes	No	No
Product	Alkyl halide	Dihalide / halohydrin	Alcohol	Alcohol	Alcohol
Reversible?	No	No	Yes	No	No
Key reagent	HCl, HBr, HI	Br_2 / Cl_2	H_2SO_4 / H_2O	$Hg(OAc)_2$; $NaBH_4$	BH_3; H_2O_2/NaOH

*Markovnikov OH regiochemistry applies in halohydrin formation (Br_2/H_2O).

The Big Picture: Choosing Your Reaction

The five reactions span two outcomes: alkyl halides and alcohols. For the three alcohol-forming reactions, the choice comes down to three questions:

What do you need?	Use this reaction
Markovnikov alcohol; rearrangement acceptable	Acid-catalyzed hydration (H_2SO_4/H_2O)
Markovnikov alcohol; NO rearrangement	Oxymercuration-demercuration ($Hg(OAc)_2/H_2O$ then $NaBH_4$)
Anti-Markovnikov alcohol; syn stereochemistry	Hydroboration-oxidation (BH_3 then H_2O_2/NaOH)
Alkyl halide (Markovnikov)	Hydrohalogenation (HX)
Vicinal dihalide (anti addition)	Halogenation (Br_2 or Cl_2)

Conclusion

Master the mechanism of each reaction, not just the product. Identify the intermediate, determine whether rearrangements are possible, and always address stereochemistry. The pattern across all five reactions is clear: when a carbocation forms (hydrohalogenation, acid hydration), expect Markovnikov regiochemistry, possible rearrangements, and racemization. When a cyclic bridged intermediate forms

(halonium, mercurinium) or no intermediate forms at all (hydroboration), the reaction is more controlled, stereospecific, and predictable.

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