Alkene Oxidation and Reduction: Complete Study Guide

This guide covers seven reactions that transform alkenes by breaking or modifying the π bond: dihydroxylation with OsO_4, ozonolysis, catalytic hydrogenation, epoxidation, epoxide ring opening, oxidative cleavage with hot concentrated $KMnO_4$, and heat of hydrogenation as a measure of alkene stability. For electrophilic addition reactions (HX, Br_2, H_2O) see the companion guide: Alkene Addition Reactions. Drawing on Clayden, Wade, McMurry, Chemistry LibreTexts, and primary literature.

Reaction	Reagent(s)	What Happens to C=C	Product(s)
Dihydroxylation	OsO_4 + NMO (cat.)	C=C → C–C; both OH same face	Syn diol (1,2-diol)
Ozonolysis (reductive)	1) O_3 2) Me_2S or PPh_3	C=C completely cleaved	Aldehydes and/or ketones
Ozonolysis (oxidative)	1) O_3 2) H_2O_2	C=C completely cleaved	Carboxylic acids and/or ketones
Catalytic hydrogenation	H_2 + Pd/C (or Pt, Ni)	C=C → C–C; 2 H added syn	Alkane
Epoxidation	mCPBA (peracid)	C=C → epoxide (3-membered ring)	Epoxide (oxirane)
Epoxide opening (acid)	H_3O^+ + Nu	Epoxide C–O opens; Nu at more subst. C	1,2-difunctional compound
Epoxide opening (base)	Nu^- (NaOH, $LiAlH_4$)	Epoxide C–O opens; Nu at less subst. C	1,2-difunctional compound
Hot conc. $KMnO_4$	$KMnO_4$ (hot, conc., acid)	C=C cleaved; maximally oxidized	Carboxylic acids and/or ketones

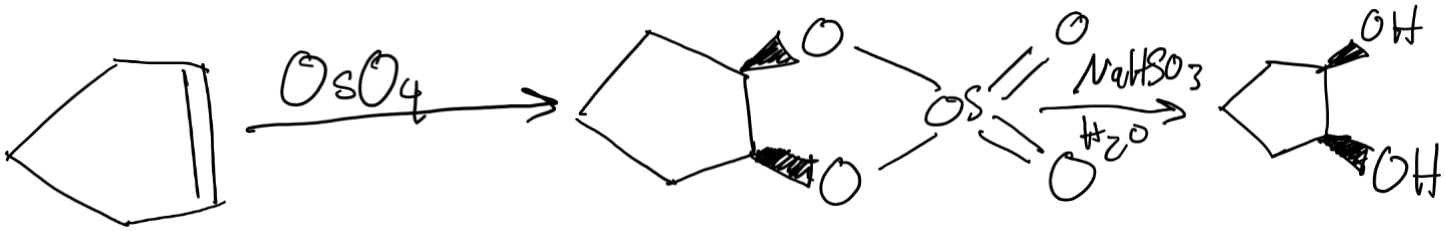
Part 1: Dihydroxylation with Osmium Tetroxide (OsO_4)

Osmium tetroxide oxidizes alkenes to vicinal diols by delivering two hydroxyl groups to the same face of the double bond in a single concerted step.

- Reaction type: Oxidative syn dihydroxylation
- Reagent: OsO_4 alone, then reductive workup ($NaHSO_3$ or Na_2SO_3)
- Product: Syn diol (both OH groups on the same face)
- Stereochemistry: Syn addition — concerted mechanism; no carbocation; no rearrangements

Mechanism: Concerted [3+2] Cycloaddition

OsO_4 reacts with the alkene in a concerted step forming a cyclic osmate ester. Both C–O bonds form simultaneously from the same face. Hydrolysis releases the syn diol and reduced osmium.



> The concerted mechanism is why both OH groups are always on the same face. Contrast with halogenation (anti addition via bromonium ion) — OsO_4 gives the opposite stereochemical outcome.

Conditions	Reagents
Stoichiometric OsO_4	OsO_4 (1 equiv) then $NaHSO_3$
Upjohn (catalytic)	Cat. OsO_4 + NMO, acetone/H_2O
Sharpless AD (asymmetric)	K_2OsO_4 + $K_3[Fe(CN)_6]$ + AD-mix

Quick Recap — OsO_4 Dihydroxylation

✓ Syn addition — both OH groups on the same face

✓ Concerted [3+2]; no rearrangements

✓ Upjohn conditions (OsO_4 + NMO) most commonly used in lab

✗ OsO_4 is toxic and volatile — always use fume hood

✗ Don’t confuse with halogenation (anti addition)

Part 2: Ozonolysis — Oxidative Cleavage of the C=C Bond

Ozonolysis treats an alkene with O_3 then a workup step, completely cleaving the C=C bond. Each carbon becomes a separate carbonyl compound. The workup determines whether aldehydes/ketones or carboxylic acids are formed.

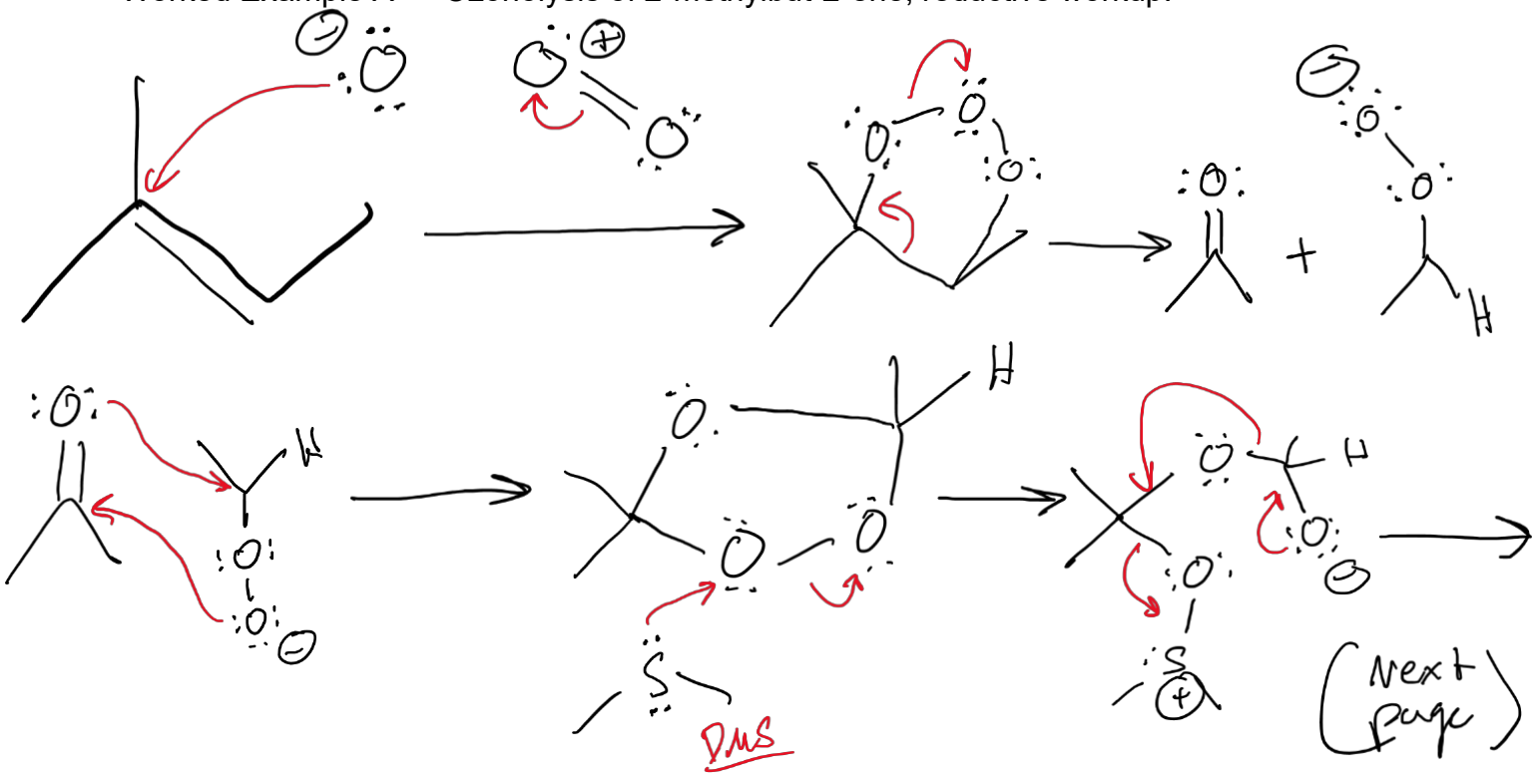
- Step 1 reagent: O_3 in CH_2Cl_2 at −78°C
- Reductive workup: Me_2S, PPh_3, or Zn/H_2O → aldehydes and/or ketones
- Oxidative workup: H_2O_2 → carboxylic acids (from CHR carbons) and/or ketones
- The C=C is completely broken — the two carbons end up in separate molecules

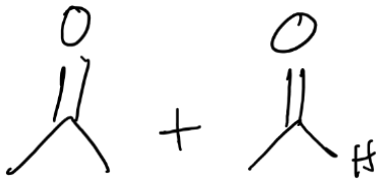
Mechanism and Product Prediction

Carbon of C=C	Reductive workup (Me_2S)	Oxidative workup (H_2O_2)
=CH_2 (terminal)	Formaldehyde (HCHO)	CO_2 + H_2O
=CHR (one substituent)	Aldehyde (R–CHO)	Carboxylic acid (R–COOH)
=CR_2 (fully substituted)	Ketone ($R_2C=O$)	Ketone ($R_2C=O$) — unchanged

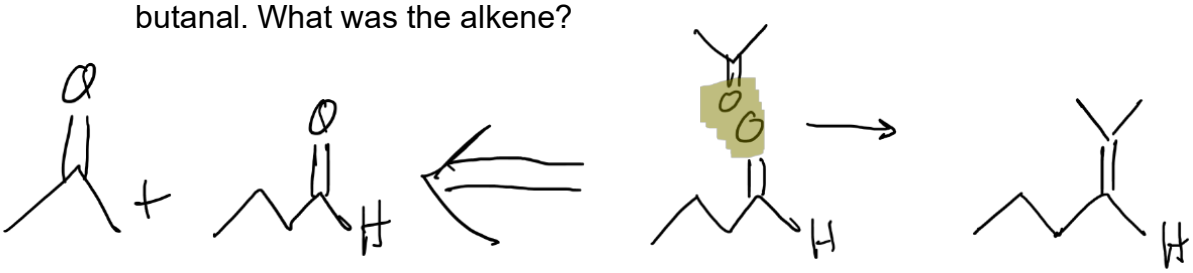
> Ketones are NOT oxidized further by H_2O_2 because there is no H on the carbonyl carbon. This is the key rule: aldehydes → acids; ketones → stay as ketones, regardless of workup.

Worked Example A — Ozonolysis of 2-methylbut-2-ene, reductive workup:





Worked Example B — Working backward: ozonolysis (reductive) gives acetone + butanal. What was the alkene?



Quick Recap — Ozonolysis

- ✓ C=C completely cleaved — each carbon becomes a carbonyl compound
- ✓ =CHR → aldehyde (reductive) or carboxylic acid (oxidative)
- ✓ $=CR_2$ → ketone in either workup
- ✓ Use reverse ozonolysis to determine double bond location in an unknown
- ✗ Ketones are NOT further oxidized — no H on carbonyl C
- ✗ Run at −78°C — ozone and ozonides are explosive at room temperature

Part 3: Catalytic Hydrogenation (Reduction of Alkenes)

Catalytic hydrogenation adds H_2 across the double bond to give an alkane. The reaction occurs on a metal catalyst surface via a syn addition mechanism.

- Reagents: H_2 gas + Pd/C, PtO_2 (Adams' catalyst), or Raney Ni
- Product: Alkane
- Stereochemistry: Syn addition — both H atoms from the same face of the catalyst surface
- No ionic intermediates; surface mechanism; catalyst is regenerated

Mechanism and Stereochemistry

Catalyst	Notes
Pd/C	Most commonly used; also removes Cbz protecting groups and hydrogenolyzes C–X bonds
PtO_2 (Adams')	More reactive; reduces hindered alkenes; can reduce aromatic rings under forcing conditions
Raney Ni	Cheap; industrial use; also desulfurizes C–S bonds
Wilkinson's (homogeneous)	$RhCl(PPh_3)_3$; selective for less hindered alkenes; does not reduce aromatics

Quick Recap — Catalytic Hydrogenation

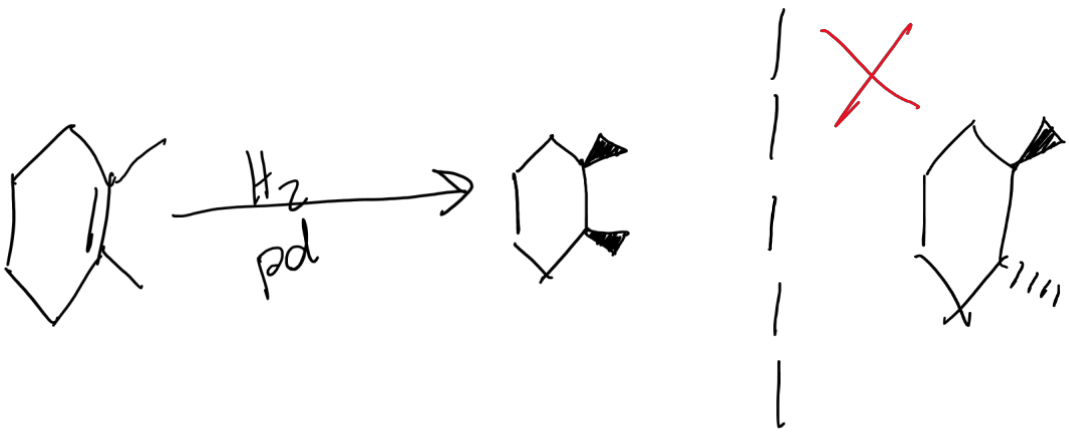
✓ H_2 + metal catalyst (Pd/C, PtO_2, Ni) reduces alkene → alkane

✓ Syn addition — both H from same face of catalyst surface

✓ More substituted alkenes react more slowly (steric access to surface)

✗ Does not reduce C=O under standard conditions

✗ Pd/C can hydrogenolyze C–X bonds — watch for halogenated substrates



Part 4: Heat of Hydrogenation and Alkene Stability

The heat of hydrogenation (ΔH°hydr) measures the enthalpy released when an alkene is hydrogenated to an alkane. Because all alkenes of the same carbon number give the same alkane, comparing ΔH°hydr values directly measures relative alkene stability.

> *More negative ΔH°hydr = less stable alkene. Less negative ΔH°hydr = more stable alkene.*

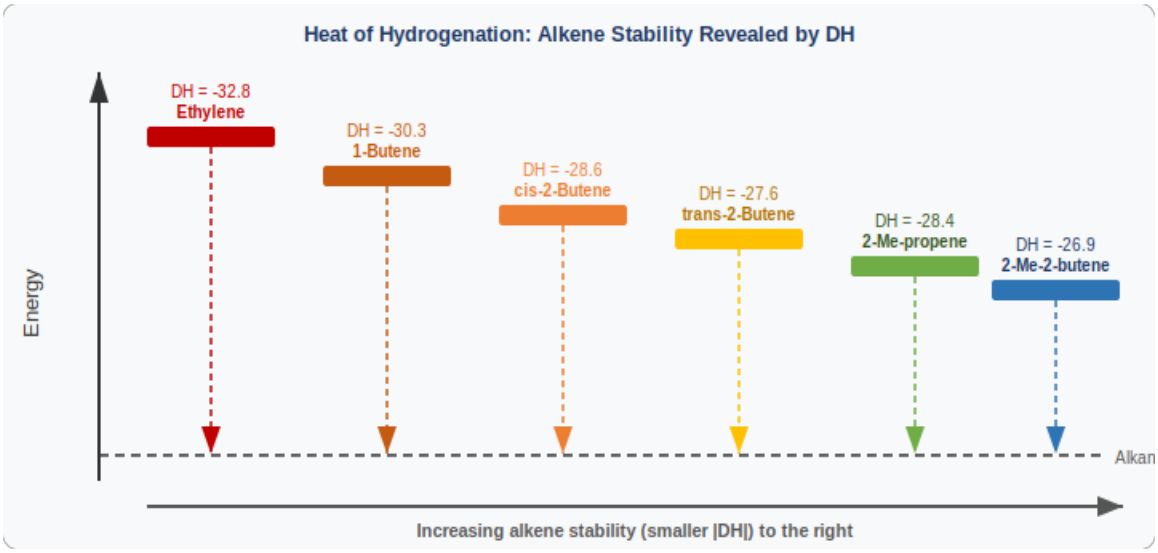


Figure 5. Heat of hydrogenation: more stable alkenes release less heat, confirming the substitution stability order.

Alkene	ΔH°hydr (kcal/mol)
Ethylene	−32.8
1-Butene (monosubstituted)	−30.3
cis-2-Butene (disubstituted)	−28.6
trans-2-Butene (disubstituted)	−27.6
2-Methyl-2-butene (trisubstituted)	−26.9
2,3-Dimethyl-2-butene (tetrasubstituted)	−26.6

- Each additional alkyl group lowers |ΔH°hydr| by ~1–2 kcal/mol — hyperconjugative stabilization measured directly.
- trans (E) > cis (Z) in stability — confirmed by ΔH°hydr (cis-2-butene releases 1.0 kcal/mol more than trans).

- Conjugated dienes have lower per-bond ΔH°hydr than isolated dienes — resonance delocalization stabilizes the π system.

> Heat of hydrogenation is a thermodynamic (stability) measurement, not a kinetic one. It tells you about the ground-state energy of the alkene, not how fast it reacts.

Quick Recap — Heat of Hydrogenation

✓ More negative ΔH°hydr = less stable starting alkene

✓ More substituted = more stable = smaller |ΔH°hydr|

✓ trans more stable than cis for same alkene — measured difference is steric strain

✗ Don’t confuse with activation energy — this is ground-state thermodynamics

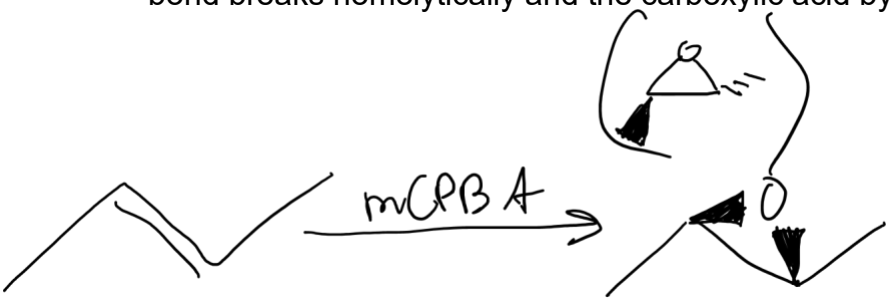
Part 5: Epoxidation of Alkenes

Epoxidation converts an alkene into an epoxide (oxirane) — a strained three-membered ring containing one oxygen atom. Epoxides are among the most useful intermediates in organic synthesis because their ring strain makes them highly reactive toward nucleophilic opening. The reaction is performed with a peracid, most commonly meta-chloroperoxybenzoic acid (mCPBA).

- Reaction type: Electrophilic oxygen transfer (concerted)
- Reagent: mCPBA (meta-chloroperoxybenzoic acid) in CH_2Cl_2, or peracetic acid (CH_3CO_3H), or MMPP
- Product: Epoxide (three-membered cyclic ether)
- Byproduct: The corresponding carboxylic acid (mCBA from mCPBA)
- Stereochemistry: Syn addition — the oxygen is delivered to one face of the alkene; alkene geometry is preserved in the epoxide
- No carbocation intermediate — no rearrangements
- Reactivity: More electron-rich alkenes react faster (more substituted → more reactive toward electrophilic O transfer)

Mechanism: Concerted Butterfly Oxygen Transfer

The peracid delivers its terminal oxygen atom to the alkene through a concerted, single-step mechanism often depicted as a ‘butterfly’ transition state. The electrophilic oxygen of the O–O bond in the peracid attacks the π system simultaneously while the O–O bond breaks homolytically and the carboxylic acid byproduct departs.



> The concerted mechanism means alkene geometry is directly transferred to the epoxide. A cis-alkene gives a cis-epoxide (the two substituents are on the same face as the O bridge). A trans-alkene gives a trans-epoxide. This is a common stereochemistry exam question.

Reactivity Trend

The peracid is an electrophilic oxidant — it reacts with the electron-rich π bond. More electron-rich alkenes react faster:

Tetrasubstituted > trisubstituted > disubstituted > monosubstituted > unsubstituted alkene

Electron-withdrawing groups on the alkene slow epoxidation significantly. α,β-unsaturated carbonyl compounds (enones) are essentially unreactive toward mCPBA because the carbonyl withdraws electron density from the double bond.

Quick Recap — Epoxidation

- ✓ mCPBA (peracid) + alkene → epoxide + carboxylic acid byproduct
- ✓ Syn addition — alkene geometry is preserved in the epoxide (cis → cis; trans → trans)
- ✓ Concerted mechanism — no carbocation; no rearrangements
- ✓ More substituted alkene reacts faster (more electron-rich π bond)
- ✓ Sharpless asymmetric epoxidation for enantioselective epoxidation of allylic alcohols
- ✗ Enones (α,β-unsaturated carbonyls) are unreactive toward mCPBA
- ✗ Don’t confuse the epoxide (3-membered ring) with the diol from OsO_4

Part 6: Epoxide Ring Opening

Epoxides are highly strained three-membered rings (ring strain ~27 kcal/mol) and are consequently much more reactive than ordinary ethers. They can be opened by a wide range of nucleophiles under either acidic or basic conditions. The conditions determine which carbon the nucleophile attacks, making regiochemistry the central issue.

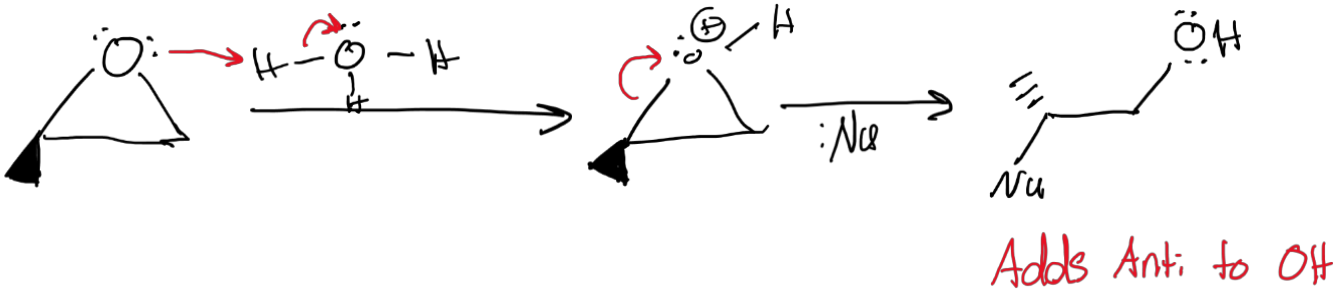
- Both acid and base conditions give anti addition overall (nucleophile attacks from the face opposite the departing oxygen)
- The key difference is which carbon is attacked: acid → more substituted carbon; base → less substituted carbon
- Common nucleophiles: H_2O, ROH, RNH_2, X^-, CN^-, H^- (from $LiAlH_4$ or $NaBH_4$), RMgX (Grignard)

Mechanism: Acid vs Base Conditions

Acid Conditions (H_3O^+ + Nu)

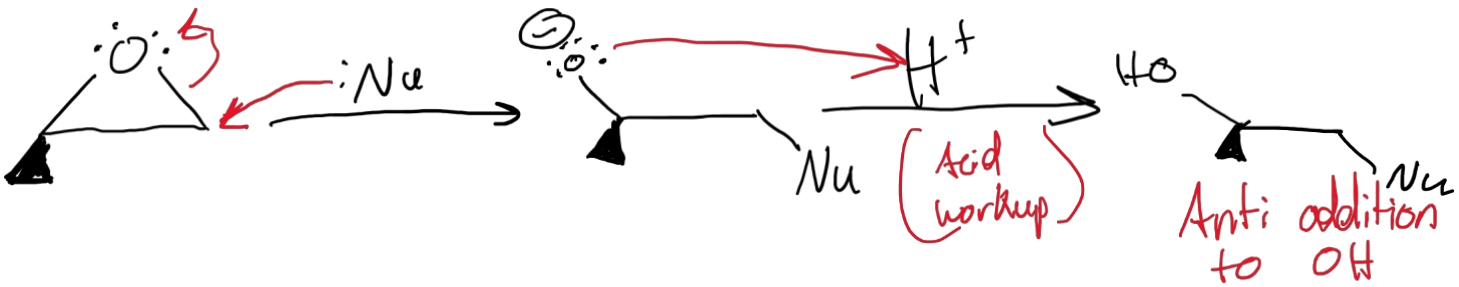
Under acidic conditions, the epoxide oxygen is first protonated by H_3O^+, which activates the ring toward nucleophilic attack. Protonation places positive charge development on the more substituted carbon (which better stabilizes partial positive charge, analogous to carbocation stability). The nucleophile then attacks the more electrophilic (more substituted) carbon from the backside.

Acid: O protonated first → more substituted C more electrophilic → Nu attacks there (Markovnikov-like)



Base Conditions (Nu^-)

Under basic conditions, the nucleophile attacks the epoxide directly without protonation of oxygen. This is an SN2-like process: the nucleophile attacks the less hindered (less substituted) carbon from the backside, causing inversion of configuration at that center. The alkoxide product is then protonated by water.



Base: Nu^- attacks directly (SN2-like) → less substituted C attacked (anti-Markovnikov; less hindered)

Both acid and base conditions give ANTI addition because the nucleophile always attacks from the face opposite the oxygen (backside attack). The difference is only in which carbon is attacked. This is a very commonly tested point on exams.

Synthetic Utility of Epoxide Opening

The combination of epoxidation (Part 5) and epoxide ring opening is extremely powerful synthetically. From a single alkene, you can install two different functional groups on adjacent carbons with complete control of regiochemistry and stereochemistry:

Quick Recap — Epoxide Ring Opening

- ✓ Epoxides open with anti addition — Nu always attacks from opposite face to O
- ✓ Acid conditions → Nu at MORE substituted C (protonation activates; SN1-like)
- ✓ Base conditions → Nu at LESS substituted C (direct SN2 attack; less hindered)
- ✓ $LiAlH_4$ gives H^- at less substituted C (base-like, SN2)
- ✓ mCPBA then H_2O/H_3O^+ gives trans-diol — the anti isomer of OsO_4 product
- ✗ Don’t forget that both conditions give anti addition — the difference is only in WHICH C is attacked
- ✗ Don’t confuse with SN2 at a normal alkyl halide — the ring strain of the epoxide is what drives the reactivity

Part 7: Oxidative Cleavage with Hot Concentrated $KMnO_4$

Potassium permanganate ($KMnO_4$) is a strong oxidant whose reactivity with alkenes depends critically on the conditions. Under cold, dilute, basic conditions it gives a syn diol (similar to OsO_4). Under hot, concentrated, acidic conditions it cleaves the C=C bond completely and oxidizes each fragment to the maximum oxidation state possible — giving carboxylic acids or ketones, just like ozonolysis with oxidative workup.

> *Hot conc. $KMnO_4$: C=C completely cleaved; each carbon maximally oxidized → carboxylic acids and/or ketones*

- Reagents: $KMnO_4$ (conc.) in H_2SO_4 (acidic) at elevated temperature, OR $KMnO_4$ (conc.) in aqueous base with heat
- Product: Carboxylic acids (from =CHR carbons) and/or ketones (from $=CR_2$ carbons)
- Byproduct: MnO_2 (brown precipitate) — the visual indicator that oxidation has occurred
- Visual test: purple $KMnO_4$ solution turns brown/black — positive test for unsaturation

Product Prediction: Hot Concentrated $KMnO_4$

Carbon of C=C	Hot conc. $KMnO_4$ product	Cold dilute $KMnO_4$ product
$=CH_2$ (terminal, no substitution)	CO_2 + H_2O (fully oxidized)	Syn diol (C–OH kept)
=CHR (one alkyl substituent)	RCOOH (carboxylic acid)	Syn diol
$=CR_2$ (two substituents, no H)	$R_2C=O$ (ketone; no further oxidation)	Syn diol
R–CH=CH–R' (both C have 1 subst.)	RCOOH + R'COOH (two acids)	Syn diol

> The critical rule: if the alkene carbon has at least one H (=CHR or $=CH_2$), hot $KMnO_4$ oxidizes all the way to a carboxylic acid (or CO_2). If the alkene carbon has NO H ($=CR_2$), it stops at the ketone — there is no H to abstract for further oxidation.

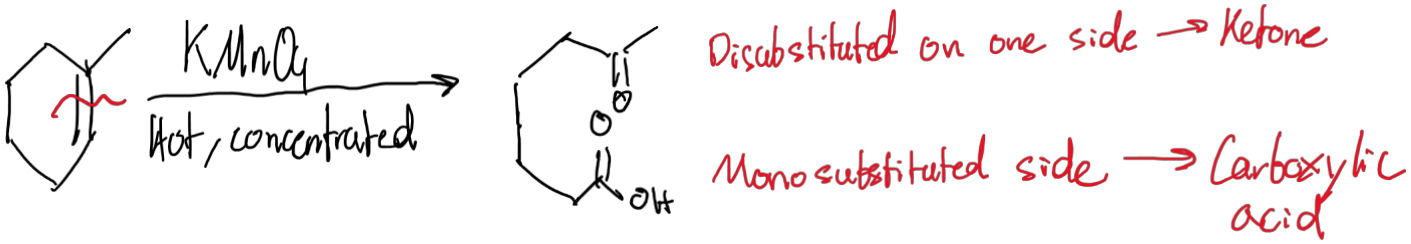
Conditions Matter: Cold Dilute vs Hot Concentrated $KMnO_4$

Conditions	Reagent

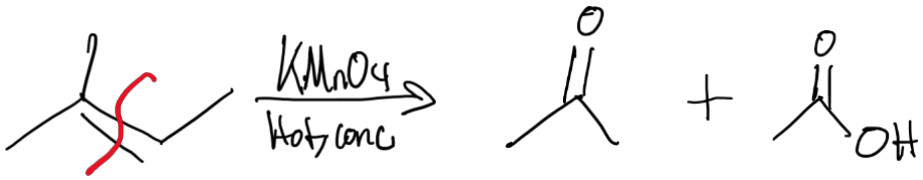
Cold, dilute, basic	$KMnO_4$ (aq., NaOH, 0°C)
Hot, concentrated, acidic	$KMnO_4$ (conc., H_2SO_4, Δ)

Worked Examples

Example A — Hot $KMnO_4$ on 1-methylcyclohexene



Example B — Hot $KMnO_4$ on 2-methylbut-2-ene



$KMnO_4$ as a Test for Unsaturation

The purple color of $KMnO_4$ solution disappears when it reacts with an alkene (or alkyne, or aldehyde), producing brown MnO_2 precipitate. This is the Baeyer test for unsaturation, a classic qualitative test still used in organic chemistry laboratory courses:

Purple $KMnO_4$ + alkene → Brown/black MnO_2 precipitate = positive test for C=C (or C≡C)

The Baeyer test is not specific — aldehydes and some other easily oxidized groups also decolorize $KMnO_4$. It confirms the presence of an oxidizable group, not necessarily a C=C specifically.

Quick Recap — Hot Concentrated $KMnO_4$

- ✓ Hot conc. $KMnO_4$ cleaves C=C completely — same overall outcome as ozonolysis with oxidative workup
- ✓ =CHR → carboxylic acid (RCOOH)
- ✓ $=CR_2$ → ketone ($R_2C=O$; not oxidized further)

✓ $=CH_2 \rightarrow CO_2 + H_2O$ (terminal carbon fully oxidized)

✓ Purple $KMnO_4 \rightarrow$ brown MnO_2: positive Baeyer test for unsaturation

✗ Cold dilute $KMnO_4$ gives syn diol, NOT cleavage — conditions are critical

✗ Don’t confuse with ozonolysis reductive workup (aldehydes, not acids)

Master Comparison: All Seven Reactions

Reaction	Reagent(s)	What Happens to C=C / Product
OsO_4 Dihydroxylation	OsO_4 + NMO (cat.)	C=C → C–C; syn diol (both OH same face)
Ozonolysis (reductive)	1) O_3 2) Me_2S	C=C cleaved → aldehydes + ketones
Ozonolysis (oxidative)	1) O_3 2) H_2O_2	C=C cleaved → carboxylic acids + ketones
Catalytic Hydrogenation	H_2 + Pd/C	C=C → alkane; syn addition of both H
Epoxidation	mCPBA	C=C → epoxide; syn O delivery; geometry preserved
Epoxide opening (acid)	H_3O^+ + Nu	Epoxide → 1,2-product; Nu at more subst. C (anti)
Epoxide opening (base)	Nu^- + H_2O	Epoxide → 1,2-product; Nu at less subst. C (anti)
Hot conc. $KMnO_4$	$KMnO_4$, H_2SO_4, Δ	C=C cleaved → carboxylic acids + ketones
Cold dilute $KMnO_4$	$KMnO_4$, NaOH, 0°C	C=C → C–C; syn diol (like OsO_4)

Key distinctions to keep straight for exams:

- Syn diol: OsO_4 or cold dilute $KMnO_4$. Anti diol: mCPBA then H_2O/H_3O^+ (epoxide opening).
- Cleavage to aldehydes/ketones: ozonolysis reductive workup. Cleavage to acids/ketones: ozonolysis oxidative workup, OR hot conc. $KMnO_4$.
- Reduction to alkane: catalytic hydrogenation (H_2 + metal catalyst).
- Epoxidation preserves alkene geometry; mCPBA is the standard reagent.

References & Further Reading

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