ORGANIC CHEMISTRY

REAGENT MASTER REFERENCE

10 Clusters | 65+ Reagents | Strength · Selectivity · Does NOT · Trap Points

CLUSTER INDEX

#	Cluster	Key Reagents
1	OXIDIZING AGENTS	PCC (CrO_2Cl·py / CH_2Cl_2), $K_2Cr_2O_7$ / H^+ (Jones reagent), $KMnO_4$ (cold, dilute), $KMnO_4$ (hot, conc.), CrO_3 / H_2SO_4 / acetone, SeO_2 (Riley oxidation), mCPBA / peracid, HIO_4 (periodic acid), Tollens reagent ($Ag[NH_3]_2^+$), Fehling / Benedict solution
2	REDUCING AGENTS	$NaBH_4$, $LiAlH_4$, H_2 / Pd-C, H_2 / Pd-$BaSO_4$ + quinoline-S (Rosenmund), H_2 / Lindlar catalyst (Pd/$CaCO_3$ + quinoline), Na / liquid NH_3 (Birch reduction), Zn(Hg) / conc. HCl (Clemmensen), N_2H_4 / KOH / ethylene glycol, heat (Wolff-Kishner), $SnCl_2$ / HCl → H_2O (Stephen reduction), $Al(OiPr)_3$ (MPV reduction), Na / ethanol (Bouveault-Blanc), $Al(OtBu)_3$ + acetone (Oppenauer)
3	HALOGENATING AGENTS	Cl_2 / hν, Br_2 / hν (or heat), NBS / hν or ROOR, CCl_4, Br_2 / CCl_4 (dark), Br_2 / $FeBr_3$ or Cl_2 / $FeCl_3$, HBr / peroxide (Kharasch), HBr / HCl / HI (ionic), $SOCl_2$, PCl_3 / PCl_5 / PBr_3
4	BASES AND ELIMINATION REAGENTS	aq. KOH (dilute), alc. KOH (conc.), NaOEt / NaOMe, $NaNH_2$ (sodamide), t-BuOK (potassium t-butoxide)
5	AROMATIC / EAS REAGENTS	HNO_3 + H_2SO_4 (mixed acid), SO_3 / H_2SO_4 (fuming), $AlCl_3$ + RX (FC alkylation), $AlCl_3$ + RCOCl (FC acylation), CO + HCl + $AlCl_3$ (Gattermann-Koch), HCN + HCl + $ZnCl_2$ (Gattermann), $CHCl_3$ + KOH (Reimer-Tiemann), CO_2 + NaOPh, 125°C, pressure (Kolbe-Schmitt), $NaNO_2$ + HCl, 0-5°C (diazotisation)
6	CARBON-CARBON BOND FORMING REAGENTS	RMgX (Grignard reagent), RLi (organolithium), R_2CuLi (Gilman reagent), KCN / NaCN, 2Na metal + 2RX (Wurtz), Zn + α-bromo ester + carbonyl (Reformatsky)
7	HALOGENATING AGENTS FOR FUNCTIONAL GROUP CONVERSION	$SOCl_2$ (thionyl chloride), PCl_3, PCl_5, PBr_3, HBF_4 + diazonium (Balz-Schiemann)
8	SPECIAL AND NAMED REAGENTS	NaCN / Thiamine (Benzoin), Anhydrous RCOONa + Ac_2O (Perkin), $PhNHNH_2$ (phenylhydrazine), FDNB / Sanger's reagent, PhNCS / Edman's reagent, DCC (dicyclohexylcarbodiimide), $Na_2[Fe(CN)_5NO]$ (sodium nitroprusside), Millon's reagent ($Hg(NO_3)_2/HNO_3$), Resorcinol + HCl (Seliwanoff), Cu-acetate / acetic acid (Barfoed)
9	DEHYDRATING AND CONDENSATION REAGENTS	Conc. H_2SO_4 (heat), H_3PO_4 (conc.), P_2O_5, Al_2O_3 (alumina, heat), Anhydrous Na-acetate + Ac_2O (Perkin), $Ba(OH)_2$ (dilute), Ac_2O (acetic anhydride)
10	KEY LOGIC SUMMARY AND DECISION	Universal Decision Rule, Oxidation state check, Solvent rule for SN vs E, Catalyst poisoning logic

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

	FRAMEWORK	

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com

CLUSTER 1: OXIDIZING AGENTS

Core Logic: Increase oxidation state of carbon. Strength determines how far oxidation goes.

A. Overview

- Oxidation ladder (weakest → strongest): PCC < $K_2Cr_2O_7$ < $KMnO_4$
- Key decision: Do you need to STOP at aldehyde (PCC) or go to acid ($K_2Cr_2O_7$/$KMnO_4$)?
- Cold vs Hot $KMnO_4$ give completely different products — conditions are part of the reagent
- Tollens and Fehling are mild oxidisers — only aldehydes, not alcohols

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
PCC (CrO_2Cl·py / CH_2Cl_2)	Mild Cr(VI)	1° alcohol → aldehyde (STOPS). 2° alcohol → ketone	Does NOT oxidise aldehyde → acid. Anhydrous — no water	Use when aldehyde is the target. Never use aqueous conditions
$K_2Cr_2O_7$ / H^+ (Jones reagent)	Moderate Cr(VI)	1° alcohol → acid. 2° alcohol → ketone	Over-oxidises 1° alcohol past aldehyde to acid	Cannot stop at aldehyde. PCC is the alternative for that
$KMnO_4$ (cold, dilute)	Mild oxidant	Alkene → vicinal diol (glycol). Baeyer's test	Does NOT cleave C=C at cold conditions	Purple → colourless/brown = positive Baeyer's test for unsaturation
$KMnO_4$ (hot, conc.)	Strong oxidant	Alkene → cleavage products. $ArCH_3$ → ArCOOH	Cleaves C=C completely. Destroys aldehyde → CO_2	Completely different from cold $KMnO_4$ — conditions define the reaction
CrO_3 / H_2SO_4 / acetone	Strong Cr(VI)	1° alcohol → acid. 2° alcohol → ketone	Similar to $K_2Cr_2O_7$ but more vigorous	Jones oxidation — harsh, not selective for sensitive substrates
SeO_2 (Riley oxidation)	Selective oxidant	Allylic/benzylic CH_2 → carbonyl	Does NOT oxidise non-activated C-H bonds	Selective for position ADJACENT to C=C. Ene mechanism
mCPBA / peracid	Peracid	Ketone → ester (Baeyer-Villiger). Alkene → epoxide	Migration aptitude: 3° > 2° > 1° > phenyl > methyl	O insertion into C-C bond. Group anti-periplanar to O-O migrates
HIO_4 (periodic acid)	Selective cleavage	Vicinal diol → 2 carbonyl fragments. α-hydroxy ketone → acid + ketone	Does NOT cleave non-adjacent OH groups	Quantitative — 1 mol HIO_4 per C-C bond between adjacent OH groups
Tollens reagent ($Ag[NH_3]_2^+$)	Mild oxidant	Aldehyde → silver mirror. Terminal alkyne → white AgC≡CR ppt	Ketones: negative. Benzaldehyde: positive	Two types of positive: mirror (aldehyde) vs white ppt (alkyne) — different chemistry

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

Fehling / Benedict solution	Cu^{2+} complex	Aliphatic aldehyde → brick red Cu_2O ppt	Aromatic aldehydes (benzaldehyde): NEGATIVE. Ketones: negative	Benedict = single stable solution (citrate). Fehling = two solutions mixed fresh (tartrate)

C. Trap Points

- **1. PCC vs $K_2Cr_2O_7$: PCC stops at aldehyde. $K_2Cr_2O_7$ goes to acid. This is the most tested oxidation MCQ**
- **2. Cold $KMnO_4$ = syn dihydroxylation (glycol). Hot $KMnO_4$ = cleavage. NEVER confuse these two**
- **3. Fehling negative for benzaldehyde. Tollens positive for benzaldehyde — aromatic aldehydes distinguish the two**
- **4. Periodic acid: α-hydroxy ketone also cleaved (not just diol) → gives acid + ketone as products**
- **5. SeO_2 oxidises allylic C-H, NOT the double bond itself**

SCAN TO VERIFY

CLUSTER 2: REDUCING AGENTS

Core Logic: Decrease oxidation state of carbon. Strength determines which functional groups are reduced.

A. Overview

- Reduction ladder (mildest → strongest): $NaBH_4$ < H_2/Pd < $LiAlH_4$
- $NaBH_4$: only C=O (aldehyde/ketone). Does NOT touch C=C, acids, esters
- $LiAlH_4$: universal — reduces everything including acids, esters, amides, nitriles
- H_2/Pd: reduces C=C and $ArNO_2$. Catalyst poisoning controls selectivity
- Named reductions (Clemmensen, Wolff-Kishner) convert C=O → CH_2 — neither is a simple hydride

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
$NaBH_4$	Mild hydride	Aldehyde/ketone → alcohol	Does NOT reduce: C=C, COOH, ester, amide, nitrile	Selective — use when C=C must survive. Safe in protic solvents
$LiAlH_4$	Strong hydride	All C=O → alcohol. COOH → 1° alcohol. Ester → 2 alcohols. Nitrile → amine. Amide → amine	Reacts violently with water — anhydrous ether only	Universal reducer. Cannot use with acid/water — destroyed immediately
H_2 / Pd-C	Catalytic	Alkene → alkane. $ArNO_2$ → $ArNH_2$. Alkyne → alkene (with Lindlar) or alkane	Normal Pd reduces C=C and nitro. Does NOT reduce isolated C=O	Selectivity: C=C > C=O. Aromatic ring NOT reduced under normal conditions
H_2 / Pd-$BaSO_4$ + quinoline-S (Rosenmund)	Poisoned catalyst	Acyl chloride → aldehyde (STOPS)	Poison prevents over-reduction to alcohol. Only acyl chloride works	Poison = quinoline-SULPHUR specifically. Un-poisoned Pd gives alcohol
H_2 / Lindlar catalyst (Pd/$CaCO_3$ + quinoline)	Selective	Alkyne → cis-alkene (syn addition)	Does NOT reduce to alkane. Stops at alkene	Gives Z (cis) alkene — syn H_2 addition. Na/NH_3 gives trans alkene
Na / liquid NH_3 (Birch reduction)	Dissolving metal	Arene → 1,4-cyclohexadiene. EDG: double bonds at unsubstituted C. EWG: at substituted C	Proton source (ROH) required. Without it, dianion forms	Naphthalene: only ONE ring reduced at 1,4-positions
Zn(Hg) / conc. HCl (Clemmensen)	Acid conditions	C=O → CH_2 (complete deoxygenation)	Fails for acid-sensitive substrates	Cannot use if substrate degrades in acid. Use Wolff-Kishner instead
N_2H_4 / KOH / ethylene glycol,	Basic conditio	C=O → CH_2 via hydrazone	Fails for base-sensitive	Complementary to Clemmensen. Choose

SCAN TO VERIFY

heat (Wolff-Kishner)	ns	intermediate	substrates. Huang-Minlon: one-pot modification	based on substrate sensitivity
$SnCl_2$ / HCl → H_2O (Stephen reduction)	Mild reductant	Nitrile → aldehyde (via aldimine intermediate)	Does NOT go to amine. Sn(II) is mild	Complementary to Rosenmund — both give aldehyde from different substrates
$Al(OiPr)_3$ (MPV reduction)	Hydride transfer	Ketone/aldehyde → alcohol (selective)	Does NOT reduce C=C bonds	6-membered cyclic TS. Oppenauer oxidation is the exact reverse
Na / ethanol (Bouveault-Blanc)	Dissolving metal	Ester → primary alcohol (2 mol per ester)	Predates $LiAlH_4$. Slower and less selective	Na/ethanol vs Na/liq.NH_3 (Birch): different solvents, different substrates
$Al(OtBu)_3$ + acetone (Oppenauer)	Hydride transfer	Secondary alcohol → ketone (reverse MPV)	Sacrificial oxidant is acetone. C=C bonds untouched	Selective for steroids and allylic alcohols

C. Trap Points

- **1. $NaBH_4$ vs $LiAlH_4$: $NaBH_4$ = ketone/aldehyde only. $LiAlH_4$ = everything. Most fundamental distinction**
- **2. Rosenmund poison: quinoline-SULPHUR (not plain quinoline). Un-poisoned Pd over-reduces to alcohol**
- **3. Clemmensen vs Wolff-Kishner: acid-sensitive substrate → use WK. Base-sensitive → use Clemmensen**
- **4. Birch: EDG ring → double bonds at UNSUBSTITUTED positions. EWG → at substituted positions**
- **5. Stephen gives ALDEHYDE from nitrile — not amine. $SnCl_2$ is mild, does not go further**
- **6. Lindlar → Z (cis) alkene. Na/liq.NH_3 → E (trans) alkene. Both from same alkyne starting material**

SCAN TO VERIFY

CLUSTER 3: HALOGENATING AGENTS

Core Logic: Introduce halogen into molecule. Mechanism (radical/ionic/EAS) determines regioselectivity.

A. Overview

- Three mechanisms: radical (hν/peroxide), ionic (HX addition), EAS (Lewis acid catalyst)
- Radical halogenation: Cl_2/hν non-selective. Br_2/hν selective (benzylic/allylic). NBS = allylic only
- Ionic addition: Markovnikov (HX). Anti-Markovnikov only for HBr with peroxide
- EAS halogenation: $Br_2/FeBr_3$ or $Cl_2/FeCl_3$ — Lewis acid generates halogen cation

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
Cl_2 / hν	Radical	Alkane → haloalkane (non-selective)	Non-selective — attacks any C-H. Poor for synthesis	Used industrially not for selective lab synthesis
Br_2 / hν (or heat)	Radical	Benzylic/allylic position selective bromination	More selective than Cl_2 radical — Br• is less reactive	Selectivity: benzylic > allylic > 3° > 2° > 1°
NBS / hν or ROOR, CCl_4	Radical	Allylic bromination — C=C intact	Does NOT attack double bond. Maintains low [Br_2]	NBS = N-bromosuccinimide. Wohl-Ziegler reaction. Allylic radical intermediate
Br_2 / CCl_4 (dark)	Ionic addition	Alkene → vicinal dibromide (anti addition)	Decolourisation test for unsaturation. Anti addition = trans product	Electrophilic addition — bromonium ion intermediate
Br_2 / $FeBr_3$ or Cl_2 / $FeCl_3$	EAS	Aromatic ring → ArBr or ArCl	Lewis acid generates Br^+ or Cl^+. Follows directing group rules	Fe acts as Lewis acid catalyst — regenerated in reaction
HBr / peroxide (Kharasch)	Radical	Alkene → anti-Markovnikov product	ONLY HBr shows this. HCl and HI do NOT	HCl: Cl• too reactive. HI: I• too stable to add. HBr: just right
HBr / HCl / HI (ionic)	Ionic addition	Alkene → Markovnikov product	Without peroxide — ionic mechanism gives Markovnikov	Carbocation intermediate. More stable carbocation = major product
$SOCl_2$	Halogenating	Alcohol → alkyl chloride (clean)	Gaseous by-products (SO_2 + HCl) — no workup needed	Preferred over PCl_5 for lab — cleaner reaction
PCl_3 / PCl_5 / PBr_3	Halogenating	Alcohol → alkyl chloride or bromide	PCl_5 more vigorous than PCl_3	PBr_3 commonly used for alkyl bromides from

SCAN TO VERIFY

				alcohols

C. Trap Points

- **1. Kharasch (anti-Markovnikov): ONLY HBr. Never HCl or HI — mechanistic reasons, not arbitrary**
- **2. NBS: allylic C-H attacked, NOT the C=C double bond. Allylic radical is the intermediate**
- **3. Br_2/CCl_4 decolourisation: alkene test. $Br_2/FeBr_3$: EAS — completely different mechanism**
- **4. $SOCl_2$ preferred over PCl_5 for lab: gaseous by-products (no liquid waste to remove)**

SCAN TO VERIFY

CLUSTER 4: BASES AND ELIMINATION REAGENTS

Core Logic: Remove H and leaving group to form π bond. Strength and solvent determine SN vs E competition.

A. Overview

- Critical distinction: aq. KOH = substitution. alc. KOH = elimination
- Strong bulky base → E2 (anti-periplanar). Weak base → E1 (carbocation first)
- NaOEt and $NaNH_2$ are strong bases for deprotonation and alkyne formation
- Zaitsev = more substituted alkene (thermodynamic). Hofmann = less substituted (bulky base/ammonium)

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
aq. KOH (dilute)	Weak Nu / weak base	Substitution → alcohol (SN1 or SN2)	Does NOT give elimination cleanly	Solvent is aqueous — water stabilises ions, favours substitution
alc. KOH (conc.)	Strong base	Elimination → alkene (E2)	Anti-periplanar geometry required	Alcoholic solvent — non-nucleophilic, favours base-mediated elimination
NaOEt / NaOMe	Strong base (alkoxide)	E2 elimination. Also Claisen condensation base	Can also act as nucleophile (Williamson ether synthesis)	Polar aprotic with alkoxide → SN2. Polar protic → E2
$NaNH_2$ (sodamide)	Very strong base (pKa ~38)	Alkyne formation from vinyl halide. Deprotonation of terminal alkyne	Stronger than NaOEt. Deprotonates terminal alkynes (pKa ~25)	Use when NaOEt is not strong enough
t-BuOK (potassium t-butoxide)	Bulky strong base	E2 elimination → Hofmann product (less substituted alkene)	Bulky — cannot approach hindered C for SN2. Forces E2	Bulkiest common base. Gives anti-Zaitsev product

C. Trap Points

- **1. aq. KOH vs alc. KOH: the most fundamental base distinction. Solvent decides mechanism**
- **2. $NaNH_2$ used for alkyne formation — strong enough to deprotonate sp C-H (pKa ~25)**
- **3. t-BuOK = Hofmann product because base is too bulky to abstract from hindered carbon**
- **4. E2 requires strict ANTI-PERIPLANAR geometry — some stereoisomers cannot undergo E2**

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

SCAN TO VERIFY

CLUSTER 5: AROMATIC / EAS REAGENTS

Core Logic: Generate electrophile → attack ring → sigma complex → deprotonate. Always think E^+ generation.

A. Overview

- Every EAS reaction requires a distinct electrophile — identify E^+ first
- Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $FeBr_3$) generate electrophiles from reagents
- Directing groups control position: o/p directors (EDG) vs m directors (EWG)
- Halogens: deactivating BUT o/p directors — important exception

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
$HNO_3 + H_2SO_4$ (mixed acid)	Nitration	$E^+ = NO_2^+$ (nitronium ion). Benzene → nitrobenzene	H_2SO_4 protonates HNO_3 to generate NO_2^+	Classic EAS. H_2SO_4 is not consumed — regenerated
SO_3 / H_2SO_4 (fuming)	Sulphonation	$E^+ = SO_3$. Benzene → sulphonic acid	REVERSIBLE — desulphonation by dilute H_2SO_4/steam. ONLY reversible EAS	Sulphonate used as blocking group in synthesis
$AlCl_3$ + RX (FC alkylation)	Friedel-Crafts	E^+ = carbocation (R^+). Benzene → alkylbenzene	Rearrangement of carbocation possible. Multiple alkylation problem	Product activates ring → over-alkylation. Acylation avoids this
$AlCl_3$ + RCOCl (FC acylation)	Friedel-Crafts	E^+ = acylium (RCO^+). Benzene → aryl ketone	NO rearrangement. Product DEACTIVATES ring → monosubstitution only	Acylium ion stable — no rearrangement. Preferred for controlled synthesis
CO + HCl + $AlCl_3$ (Gattermann-Koch)	Formylation	$E^+ = CHO^+$ (formyl). Benzene → benzaldehyde	ONLY simple arenes. Phenol/aniline do NOT work. No HCN	Distinguish from Gattermann: CO here, HCN in Gattermann
HCN + HCl + $ZnCl_2$ (Gattermann)	Formylation	$E^+ = CHO^+$ via imine. Activated arene → aryl aldehyde	Works on phenol/aniline (activated rings). Uses HCN not CO	Key distinction: Gattermann-Koch uses CO. Gattermann uses HCN
$CHCl_3$ + KOH (Reimer-Tiemann)	Formylation of phenol	Intermediate = $:CCl_2$ (dichlorocarbene). Phenol → salicylaldehyde (o-major)	ONLY phenols. Not general EAS — carbene mechanism	Ring expansion possible (cyclohexadienone). Para product also formed
CO_2 + NaOPh, 125°C, pressure	Carboxylation of	Phenoxide → sodium salicylate → salicylic	Needs DRY sodium PHENOXIDE, not	K-salt at higher T → para product. Na-salt →

SCAN TO VERIFY

(Kolbe-Schmitt)	phenol	acid	free phenol	ortho product
$NaNO_2$ + HCl, 0-5°C (diazotisation)	Diazonium formation	$ArNH_2 \rightarrow ArN_2^+$ (diazonium salt)	Temperature critical: 0-5°C. Above 5°C — diazonium decomposes	Diazonium is intermediate for Sandmeyer, coupling, Balz-Schiemann

C. Trap Points

- **1. Sulphonation ONLY reversible EAS — all others irreversible. Blocking group strategy uses this**
- **2. FC alkylation: rearrangement always check. FC acylation: no rearrangement, monosubstitution**
- **3. Gattermann-Koch (CO) vs Gattermann (HCN): reagent is the differentiator**
- **4. Reimer-Tiemann: carbene (:CCl_2) is electrophile — NOT a carbocation. Mechanism is different**
- **5. Kolbe-Schmitt: DRY sodium PHENOXIDE mandatory. Free phenol does not work**

SCAN TO VERIFY

CLUSTER 6: CARBON-CARBON BOND FORMING REAGENTS

Core Logic: Extend carbon skeleton. Either nucleophilic C attacks electrophilic C, or coupling via metal.

A. Overview

- Three strategies: (1) organometallic Nu attacks carbonyl, (2) CN^- extension, (3) enolate chemistry
- Grignard (RMgX): most versatile C-nucleophile. Destroyed by water/acid/alcohol
- RLi: stronger than Grignard. Also destroyed by protic solvents
- KCN/NaCN: chain extension by exactly 1 carbon
- Na metal: Wurtz coupling (C-C from 2 alkyl halides)

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
RMgX (Grignard reagent)	Strong C-nucleophile	Carbonyl → alcohol. CO_2 → carboxylic acid (one C more). Ester → tertiary alcohol	Destroyed by water, acid, alcohol, O_2. Anhydrous ether only	Attacks all electrophilic carbons. Cannot coexist with acidic H
RLi (organolithium)	Stronger than Grignard	Same reactions as Grignard but more reactive. Attacks hindered carbonyls	Even more moisture-sensitive than Grignard	Used when Grignard fails due to steric hindrance
R_2CuLi (Gilman reagent)	Soft C-nucleophile	Conjugate addition (1,4) to α,β-unsaturated carbonyl. Coupling with alkyl halides	Does NOT do 1,2-addition to carbonyl. Selective for 1,4	Key selectivity: Grignard → 1,2-addition. Gilman → 1,4-addition
KCN / NaCN	C-nucleophile	RX → nitrile (chain extension +1C). Carbonyl → cyanohydrin	CN^- is both C-nucleophile and N-nucleophile — reacts via C	Cyanohydrin hydrolysis → α-hydroxy acid. Killiani-Fischer uses this
2Na metal + 2RX (Wurtz)	Radical coupling	2RX → R-R (symmetric alkane). Both halides must be same	Mixed RX gives 3 products — not useful. Cannot make odd-carbon chain from one halide	Aryl halides don't work (Fittig = ArX + ArX + 2Na → Ar-Ar)
Zn + α-bromo ester + carbonyl (Reformatsky)	Zn-enolate	β-hydroxy ester product	Zn enolate less reactive than Grignard — does NOT attack ester group	Selective: attacks only aldehyde/ketone. Use when Grignard gives side reactions

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

C. Trap Points

- **1. Grignard: anhydrous ether ONLY. Any protic source (water, alcohol, acid) destroys it immediately**
- **2. Gilman (R_2CuLi): 1,4-addition selectively. Grignard: 1,2-addition. Both are C-nucleophiles**
- **3. KCN adds C — extends chain by 1. NaCN same reagent — use when KCN unavailable**
- **4. Wurtz mixed halides: 3 products formed statistically — R-R, R-R', R'-R'. Not a useful synthesis**
- **5. Reformatsky: milder than Grignard. Does not attack ester in same molecule — selective**

SCAN TO VERIFY

CLUSTER 7: HALOGENATING AGENTS FOR FUNCTIONAL GROUP CONVERSION

Core Logic: Convert OH or COOH to halide. Choice depends on which halide and how clean the reaction must be.

A. Overview

- $SOCl_2$ preferred for lab — gaseous by-products (SO_2 + HCl) make purification trivial
- PCl_3, PCl_5: also convert OH → Cl but messier
- PBr_3: standard for alkyl bromides from alcohols
- HX can also convert alcohols but requires acid conditions — risk of elimination/rearrangement

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
$SOCl_2$ (thionyl chloride)	Chlorinating	ROH → RCl + SO_2 + HCl (gaseous by-products)	Gaseous by-products leave reaction — easy purification	Most convenient lab method for alkyl chlorides from alcohols
PCl_3	Chlorinating	ROH → RCl (milder)	Less vigorous than PCl_5	Also converts RCOOH → RCOCl (acyl chloride)
PCl_5	Chlorinating	ROH → RCl (vigorous). RCOOH → RCOCl	More vigorous than PCl_3. Can cause side reactions	Used for acid chloride formation from carboxylic acids
PBr_3	Brominating	ROH → RBr	Standard method for alkyl bromides	Also used in HVZ reaction (first step: RCOOH → RCOBr)
HBF_4 + diazonium (Balz-Schiemann)	Fluorinating	$ArN_2^+ + HBF_4$ → ArN_2BF_4 → dry pyrolysis → ArF	Only reliable method for ArF. Diazonium fluoroborate is stable solid	F^- is best leaving group in SNAr (paradox vs SN2 where F^- is worst)

C. Trap Points

- **1. $SOCl_2$ advantage: gaseous by-products (SO_2 + HCl) — no liquid waste, no aqueous workup needed**
- **2. PCl_5 vs PCl_3: PCl_5 more reactive. Both give alkyl chlorides but PCl_5 can give side reactions**
- **3. Balz-Schiemann = ONLY reliable route to ArF. Cannot use Sandmeyer with fluoride**

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

CLUSTER 8: SPECIAL AND NAMED REAGENTS

Core Logic: Reagents with unique selectivity not covered by general categories. Each has one specific use-case.

A. Overview

- These are reagents that appear in specific named reactions — learn the pairing
- Most have a narrow substrate scope — specificity is their defining feature
- Exam tests: (1) which reagent for which named reaction, (2) what does NOT work with this reagent

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
NaCN / Thiamine (Benzoin)	Umpolung catalyst	ArCHO → benzoin (α-hydroxy ketone). CN^- is catalyst, not consumed	ONLY aromatic aldehydes. Aliphatic fail	CN^- reverses polarity of carbonyl — nucleophilic catalyst (umpolung)
Anhydrous RCOONa + Ac_2O (Perkin)	Condensation	ArCHO + acid anhydride → α,β-unsaturated acid	ANHYDROUS critical — water destroys anhydride	Product always E (trans). Aliphatic aldehydes give poor yield
$PhNHNH_2$ (phenylhydrazine)	Carbonyl detection	Aldehyde/ketone → phenylhydrazone. Excess → osazone (C1+C2)	3 mol $PhNHNH_2$ for osazone. Sucrose: slow (non-reducing)	Glucose/fructose/ mannose give SAME osazone — identical C3-C6
FDNB / Sanger's reagent	N-terminus labelling	Peptide N-terminus → DNP-amino acid after hydrolysis	Destroys entire peptide — identifies N-terminus only	Nobel Prize 1958. Used for insulin sequencing
PhNCS / Edman's reagent	N-terminus sequencing	N-terminal residue → PTH-amino acid. Peptide intact for next cycle	Repetitive — one residue at a time. Peptide survives	Automated sequenators. Sanger destroys; Edman preserves
DCC (dicyclohexylcarbodiimide)	Coupling agent	Amino acid + carboxylic acid → amide/peptide bond (no water)	Used in peptide synthesis. Activates COOH without harsh conditions	DCC removed as DCU (dicyclohexylurea) by-product
$Na_2[Fe(CN)_5NO]$ (sodium nitroprusside)	Detection	(1) Thiol/SH + NH_3 → purple. (2) Active methylene + KOH → red	Two different positives — context determines which	Do not confuse: SH detection vs active methylene detection
Millon's reagent ($Hg(NO_3)_2/HNO_3$)	Protein detection	Tyrosine (phenolic OH) → red precipitate on heating	Positive for any phenol. Negative for proteins lacking tyrosine	NOT a general protein test. Biuret is general (peptide bonds)

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com

Resorcinol + HCl (Seliwanoff)	Sugar type detection	Ketose (fructose) → deep red (fast, <1 min). Aldose → faint pink (slow)	Time distinguishes: ketose fast, aldose slow	Dehydrates ketose to HMF faster than aldose → red colour with resorcinol
Cu-acetate / acetic acid (Barfoed)	Sugar type detection	Monosaccharide → red Cu_2O (within 2 min). Disaccharide: too slow	Mildly acidic — disaccharides too slow to reduce	Distinguishes monosaccharide from disaccharide — both are reducing sugars

C. Trap Points

- **1. Sanger: peptide destroyed after identification. Edman: peptide survives — can repeat for sequencing**
- **2. Seliwanoff: TIME is the differentiator. Both fructose and glucose eventually give colour — rate matters**
- **3. Sodium nitroprusside: TWO different positives. SH group with NH_3 vs active methylene with KOH**
- **4. Millon's: detects TYROSINE only — not all proteins. Biuret detects all proteins (≥2 peptide bonds)**
- **5. DCC: activates carboxyl group for peptide coupling. Removed as urea by-product — clean reaction**

SCAN TO VERIFY

CLUSTER 9: DEHYDRATING AND CONDENSATION REAGENTS

Core Logic: Remove water or drive condensation reactions. Create bonds by eliminating small molecules.

A. Overview

- Conc. H_2SO_4: dehydration of alcohols AND esterification AND sulphonation
- P_2O_5 and Al_2O_3: solid-phase dehydrating agents
- NaOEt and $Ba(OH)_2$: bases for enolate-driven condensations
- Ac_2O: acylating agent — forms esters and amides

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
Conc. H_2SO_4 (heat)	Acid dehydration	Alcohol → alkene (E1). Also: esterification, sulphonation, nitration (with HNO_3)	Temperature controls: low T → ether (SN2). High T → alkene (E1)	Versatile acid — 3 different reactions depending on conditions
H_3PO_4 (conc.)	Milder dehydration	Alcohol → alkene. Milder than H_2SO_4	Less side reactions than H_2SO_4 (no sulphonation/oxidation)	Preferred when substrate sensitive to strong oxidising conditions
P_2O_5	Solid dehydrant	Carboxylic acid → anhydride. Also general dehydration	Strong dehydrant	Used in industrial settings and for anhydride formation
Al_2O_3 (alumina, heat)	Solid dehydrant	Alcohol → alkene at high temperature	Heterogeneous — solid catalyst	Industrial dehydration. Ziegler-Natta context
Anhydrous Na-acetate + Ac_2O (Perkin)	Condensation	ArCHO + anhydride → α,β-unsaturated acid	Anhydrous critical. Base is carboxylate, not hydroxide	Generates enolate of anhydride for condensation
$Ba(OH)_2$ (dilute)	Selective Aldol base	Cross-aldol / Claisen-Schmidt: ArCHO + ketone → chalcone	Milder than NaOH. Selective for cross-condensation	Barium hydroxide preferred to avoid self-condensation
Ac_2O (acetic anhydride)	Acylating agent	Alcohol → ester (acylation). Amine → amide. Also used in Perkin reaction	Milder than acetyl chloride. Does not require anhydrous conditions	Common protecting group reagent for OH and NH_2

C. Trap Points

- **1. Conc. H_2SO_4: low T (140°C) → ether (intermolecular dehydration). High T (170°C) → alkene (intramolecular)**

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

- **2. H_3PO_4 preferred over H_2SO_4 when oxidation of substrate is a concern**
- **3. Perkin reaction: ANHYDROUS Na-acetate and anhydrous Ac_2O mandatory**

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com
Document ID · RGY-PDF-2026-001

CLUSTER 10: KEY LOGIC SUMMARY AND DECISION FRAMEWORK

Core Logic: Universal thinking: identify transformation needed → select reagent category → apply selectivity rules.

A. Overview

- OXIDATION needed: PCC (stop at aldehyde) | $K_2Cr_2O_7$ (go to acid) | $KMnO_4$ (cleavage/glycol)
- REDUCTION needed: $NaBH_4$ (ketone/aldehyde only) | $LiAlH_4$ (universal) | H_2/Pd (C=C and NO_2)
- HALOGENATION needed: $SOCl_2$ (clean) | NBS (allylic) | $Br_2/FeBr_3$ (EAS) | HBr+peroxide (anti-Markov)
- C-C BOND needed: Grignard (carbonyl) | KCN (+1C) | Wurtz (symmetric) | Reformatsky (selective)
- ELIMINATION needed: alc. KOH (E2, Zaitsev) | t-BuOK (Hofmann product) | aq. KOH (substitution)

B. Reagent Table

Reagent	Type	What it DOES	What it does NOT do	Key Exam Point
Universal Decision Rule	Function → Reagent	What transformation is needed? → Which category? → Which strength/selectivity?	Always identify: substrate + desired product + what must NOT happen	The 'Does NOT' column is as important as the 'Does' column in MCQs
Oxidation state check	Carbon oxidation	C(-4) alkane → C(-3) haloalkane → C(-1) alcohol → C(0) aldehyde/ketone → C(+2) acid	Each step up requires an oxidising agent. Each step down requires a reducing agent	Knowing oxidation state instantly tells you which class of reagent is needed
Solvent rule for SN vs E	KOH	aq. KOH → SN (substitution). alc. KOH → E (elimination)	Solvent is part of the reagent system — never ignore it	This distinction appears in >30% of alkyl halide MCQs
Catalyst poisoning logic	Selectivity control	Rosenmund: $Pd/BaSO_4$ + quinoline-S stops at aldehyde. Lindlar: $Pd/CaCO_3$ + quinoline stops at alkene	Poisoning REDUCES catalyst activity to stop at intermediate oxidation level	Without poison, H_2/Pd reduces completely — no selectivity

C. Trap Points

- **1. The 'Does NOT' information is tested as frequently as the 'Does' information in MCQs**
- **2. Solvent always part of reagent description — aq. KOH ≠ alc. KOH**

SCAN TO VERIFY

© Ram Govind Yadav · ramgovindyadav.com

- **3. Catalyst and its poison are inseparable — Rosenmund = $Pd/BaSO_4$ + quinoline-SULPHUR together**
- **4. Temperature and concentration are part of the reagent: cold $KMnO_4$ ≠ hot $KMnO_4$**

SCAN TO VERIFY