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ORGANIC

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Named Reactions — 80 Reaction Master Sheet

Every named reaction you are likely to meet, with reagents and conditions, what it does, and the trap examiners set, grouped by the kind of change it makes.

WHAT YOU WILL BE ABLE TO DO

- Name the reaction from its reagents, and the reagents from its name
- Tell look-alike pairs apart: Clemmensen vs Wolff–Kishner, Sandmeyer vs Gattermann, Saytzeff vs Hofmann
- Track carbon count: which reactions add one carbon, remove one, or double the chain
- Spot the exam trap built into each reaction before it costs you marks

INSIDE

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SECTION A

C–C bonds: coupling and organometallics

A

Join two carbon pieces. Ask: which metal, and which partner?

#	Reaction	Reagents & conditions	What it does	Exam trap
01	Wurtz	2 R–X + 2 Na, dry ether	R–R (symmetrical alkane)	Mixed halides give three alkanes; can't make CH_4; 3° halides give alkenes
02	Wurtz–Fittig	Ar–X + R–X + 2 Na, dry ether	Ar–R (alkylbenzene)	R–R and Ar–Ar form as side products
03	Fittig	2 Ar–X + 2 Na, dry ether	Ar–Ar (biphenyl)	Aryl halides only
04	Ullmann	2 Ar–I + Cu powder, heat	Ar–Ar	Copper, not sodium; iodides work best
05	Frankland	2 R–X + Zn, heat	R–R + ZnX_2	The zinc version of Wurtz
06	Corey–House	R_2CuLi (Gilman reagent) + R′–X	R–R′ (unsymmetrical alkane)	R′–X should be 1°; this is how to avoid Wurtz mixtures
07	Kolbe electrolysis	Aqueous RCOONa, electrolysis	R–R + CO_2 at anode, H_2 at cathode	Product has an even number of C; CH_4 can't be made
08	Grignard	RMgX + C=O, then H_3O^+	HCHO → 1°, RCHO → 2°, R_2CO → 3° alcohol; CO_2 → RCOOH	Strictly dry; any O–H or N–H destroys it, giving R–H
09	Reformatsky	α-Bromo ester + Zn + aldehyde/ketone, then H_3O^+	β-Hydroxy ester	Zinc enolate is mild: it doesn't attack the ester group
10	Simmons–Smith	CH_2I_2 + Zn(Cu) + alkene	Cyclopropane	Stereospecific: cis alkene gives cis cyclopropane

SECTION B

Carbonyl condensations

B

Most start with an enolate or a carbanion attacking a C=O. Check for α-hydrogens first.

#	Reaction	Reagents & conditions	What it does	Exam trap
11	Aldol	Aldehyde/ketone with α-H, dil. NaOH	β-Hydroxy carbonyl; on heating, α,β-unsaturated carbonyl	Needs α-hydrogen
12	Cross aldol	Two different carbonyls, dil. NaOH	Mixture of four products	Clean only if one partner has no α-H (HCHO, PhCHO)
13	Claisen–Schmidt	ArCHO + ketone (e.g. acetophenone), NaOH	α,β-Unsaturated ketone (chalcone)	It's a crossed aldol with an aromatic aldehyde
14	Cannizzaro	Aldehyde with no α-H + conc. NaOH	Alcohol + carboxylate salt	Disproportionation; aldehydes with α-H do aldol instead
15	Crossed Cannizzaro	HCHO + ArCHO, conc. NaOH	$HCOO^-$ + $ArCH_2OH$	HCHO is always the one oxidised
16	Benzoin condensation	2 PhCHO, KCN, aqueous ethanol	Benzoin, PhCH(OH)COPh	The catalyst is cyanide, not hydroxide
17	Perkin	ArCHO + $(RCH_2CO)_2O$ + RCH_2COONa, heat	α,β-Unsaturated acid (PhCHO → cinnamic acid)	Base is the salt of the same acid as the anhydride

#	Reaction	Reagents & conditions	What it does	Exam trap
18	Knoevenagel	Aldehyde + $CH_2(COOEt)_2$ or malonic acid, piperidine/pyridine	α,β-Unsaturated compound	A weak base is enough: the CH_2 is doubly activated
19	Claisen condensation	2 esters with α-H, NaOEt, then H_3O^+	β-Keto ester (ethyl acetate → ethyl acetoacetate)	The alkoxide base must match the ester
20	Dieckmann	1,6- or 1,7-diester, NaOEt	Cyclic β-keto ester (5- or 6-ring)	Intramolecular Claisen
21	Michael addition	Stabilised carbanion + α,β-unsaturated carbonyl, base	1,5-Dicarbonyl (1,4-addition)	Soft nucleophiles add 1,4; Grignards usually add 1,2
22	Mannich	Enolisable carbonyl + HCHO + 2° amine·HCl	β-Amino carbonyl (Mannich base)	Three components; an iminium ion is the electrophile
23	Wittig	$Ph_3P{=}CHR$ (ylide) + aldehyde/ketone	Alkene + $Ph_3P{=}O$	C=O becomes C=C at exactly that position
24	Strecker	Aldehyde + NH_4Cl + KCN, then H_3O^+	α-Amino acid	Goes through an α-aminonitrile

SECTION C

Reductions

C

Know which reagent stops where, and which works in acid or base.

#	Reaction	Reagents & conditions	What it does	Exam trap
25	Clemmensen	Zn–Hg, conc. HCl	C=O → CH_2	Acidic: avoid with acid-sensitive groups
26	Wolff–Kishner	NH_2NH_2, then KOH in ethylene glycol, heat	C=O → CH_2	Basic: the choice when the molecule can't take acid
27	Rosenmund	RCOCl + H_2, Pd/$BaSO_4$ (poisoned)	RCHO	Poison stops over-reduction to alcohol; HCHO can't be made
28	Stephen	RCN + $SnCl_2$/HCl, then H_3O^+	RCHO (via an imine)	Same carbon count as the nitrile
29	Meerwein–Ponndorf–Verley	$Al(O\text{-}iPr)_3$ in isopropanol	Aldehyde/ketone → alcohol	Selective: C=C and NO_2 untouched; reverse of Oppenauer
30	Birch	Na or Li in liquid NH_3, EtOH	Benzene → 1,4-cyclohexadiene	Partial reduction; product is no longer aromatic
31	Bouveault–Blanc	Na + absolute ethanol	Ester → two alcohols	Older alternative to $LiAlH_4$
32	Sabatier–Senderens	H_2, finely divided Ni, 523–573 K	Alkene/alkyne → alkane	Pt or Pd work at room temperature

SECTION D

Oxidations

D

Watch for the reagent that stops early and the one that cuts bonds.

#	Reaction	Reagents & conditions	What it does	Exam trap
33	Oppenauer	$Al(O\text{-}tBu)_3$, acetone	2° alcohol → ketone	Reverse of MPV; selective
34	Etard	Toluene + CrO_2Cl_2 in CS_2, then H_3O^+	Benzaldehyde	Stops at the aldehyde (chromium complex)
35	Baeyer–Villiger	Ketone + peracid (mCPBA, CH_3CO_3H)	Ester (O inserted next to C=O)	Migration: 3° > 2° ≈ aryl > 1° > CH_3; H fastest in aldehydes
36	Ozonolysis	O_3, then Zn/H_2O	C=C cut into two C=O	Zn stops H_2O_2 oxidising aldehydes to acids
37	Baeyer's test	Cold, dilute, alkaline $KMnO_4$	C=C → cis-1,2-diol; purple colour fades	Hot acidic $KMnO_4$ cleaves the C=C instead
38	Iodoform (haloform)	I_2 + NaOH	CH_3CO– or $CH_3CH(OH)$– → CHI_3 (yellow) + $RCOO^-$	Ethanol is the only 1° alcohol and ethanal the only aldehyde that respond

SECTION E

Aromatic substitution and diazonium chemistry

E

Electrophile first: name it and you can predict the product.

#	Reaction	Reagents & conditions	What it does	Exam trap
39	Friedel–Crafts alkylation	ArH + R–Cl, anhydrous $AlCl_3$	Ar–R	Carbocation rearranges; polyalkylation; fails on nitrobenzene
40	Friedel–Crafts acylation	ArH + RCOCl or $(RCO)_2O$, anhydrous $AlCl_3$	Aryl ketone	No rearrangement; ketone deactivates, so no polysubstitution
41	Gattermann–Koch	Benzene + CO + HCl, $AlCl_3$/CuCl	Benzaldehyde	Formyl chloride forms in situ
42	Reimer–Tiemann	Phenol + $CHCl_3$ + aq. NaOH, then H^+	Salicylaldehyde (ortho –CHO)	Electrophile is dichlorocarbene; with CCl_4 gives salicylic acid
43	Kolbe–Schmitt	Sodium phenoxide + CO_2, 400 K, 4–7 atm, then H^+	Salicylic acid	Electrophile is CO_2; ortho product
44	Diazotisation	$ArNH_2$ + $NaNO_2$ + HCl, 273–278 K	$ArN_2^+Cl^-$	Keep it cold; aliphatic diazonium salts decompose at once
45	Sandmeyer	ArN_2^+ + CuCl/HCl, CuBr/HBr or CuCN/KCN	ArCl, ArBr, ArCN	Copper(I) salts
46	Gattermann	ArN_2^+ + Cu powder + HX	ArCl, ArBr	Copper metal, not a Cu(I) salt
47	Balz–Schiemann	ArN_2^+ + HBF_4, then heat	ArF	The standard way to make aryl fluorides
48	Azo coupling	ArN_2^+ + phenol (mildly alkaline) or aniline (mildly acidic)	Azo dye, usually para	Phenol + benzenediazonium gives orange p-hydroxyazobenzene
49	Fries rearrangement	Phenyl ester + anhydrous $AlCl_3$	o- and p-Hydroxyaryl ketones	Low temperature favours para; high favours ortho
50	Schotten–Baumann	Phenol or amine + C_6H_5COCl, aq. NaOH	Benzoate ester or benzamide	The base removes HCl as it forms

SECTION F

Rearrangements

F

Something migrates toward an electron-poor centre. Find the cation, nitrene or isocyanate.

#	Reaction	Reagents & conditions	What it does	Exam trap
51	Beckmann	Ketoxime + H_2SO_4 or PCl_5	N-Substituted amide	Group anti to –OH migrates; cyclohexanone oxime → caprolactam (nylon-6)
52	Pinacol–pinacolone	1,2-Diol + H^+	Ketone	More stable cation forms first; then the better group migrates
53	Benzilic acid	Benzil + KOH, then H^+	Benzilic acid (α-hydroxy acid)	1,2-Diketone; aryl shift

#	Reaction	Reagents & conditions	What it does	Exam trap
54	**Claisen rearrangement**	Allyl aryl ether, heat (~200 °C)	o-Allylphenol	[3,3] sigmatropic; goes para if both ortho positions are blocked
55	**Cope rearrangement**	1,5-Diene, heat	Isomeric 1,5-diene	[3,3] sigmatropic, all-carbon version
56	**Favorskii**	α-Haloketone + OH^- or RO^-	Carboxylic acid or ester	Cyclic ketones contract by one carbon
57	**Arndt–Eistert**	RCOCl + CH_2N_2, then Ag_2O/H_2O	RCH_2COOH	Adds one CH_2 (Wolff rearrangement step)
58	**Hofmann bromamide**	$RCONH_2 + Br_2 + 4\ NaOH$	RNH_2, one carbon fewer	Isocyanate intermediate; gives only 1° amines
59	**Curtius**	Acyl azide $RCON_3$, heat; then H_2O	$R–N=C=O \rightarrow RNH_2$	Same isocyanate route as Hofmann

SECTION G

Functional-group interconversions

G

Swap one group for another; watch the carbon count.

#	Reaction	Reagents & conditions	What it does	Exam trap
60	Hell–Volhard–Zelinsky	$RCH_2COOH + Cl_2$ or Br_2, red P	α-Halo acid	Needs an α-hydrogen
61	Hunsdiecker	$RCOOAg + Br_2$ in CCl_4, heat	$R–Br + CO_2$ (one carbon fewer)	The silver salt must be dry
62	Finkelstein	R–Cl or R–Br + NaI, dry acetone	R–I	NaCl/NaBr precipitate, driving it forward
63	Swarts	R–Cl/Br + AgF, Hg_2F_2, CoF_2 or SbF_3	R–F	Metal fluorides, not NaF
64	Williamson ether	$R–O^-Na^+ + R'–X$	R–O–R′	R′–X must be 1°; for t-butyl methyl ether use $(CH_3)_3CONa + CH_3Br$
65	Gabriel phthalimide	Phthalimide + KOH; then R–X; then hydrolysis	1° aliphatic amine	Can't make aromatic amines (Ar–X won't do SN2)
66	Fischer esterification	RCOOH + R′OH, conc. H_2SO_4 (reversible)	$RCOOR' + H_2O$	The acid's C–OH bond breaks (shown by ^{18}O labelling)
67	Decarboxylation	RCOONa + soda lime (NaOH/CaO), heat	R–H (one carbon fewer)	Use the sodium salt, not the free acid

SECTION H

Additions and eliminations

H

Where does H go, where does the new group go, and can the cation rearrange?

#	Reaction	Reagents & conditions	What it does	Exam trap
68	Markovnikov addition	HX + unsymmetrical alkene	H adds to the carbon with more H	Really "via the more stable carbocation", so rearrangements can occur
69	Kharasch (peroxide effect)	HBr + alkene, organic peroxide	Anti-Markovnikov bromide	Only HBr; HCl and HI don't show it
70	Hydroboration–oxidation	B_2H_6 (BH_3·THF), then H_2O_2/OH^-	Anti-Markovnikov alcohol, syn addition	No rearrangement
71	Oxymercuration–demercuration	$Hg(OAc)_2/H_2O$, then $NaBH_4$	Markovnikov alcohol	No rearrangement, unlike acid-catalysed hydration
72	Diels–Alder	Conjugated diene (s-cis) + dienophile, heat	Cyclohexene ring	Concerted [4+2]; stereochemistry kept; endo preferred
73	Saytzeff elimination	R–X + alcoholic KOH	More substituted alkene	A bulky base gives the Hofmann product instead
74	Hofmann elimination	Quaternary ammonium hydroxide, heat	Less substituted alkene	The opposite of Saytzeff
75	Cope elimination	Tertiary amine oxide, heat	Alkene + hydroxylamine	Intramolecular, syn elimination

SECTION I

Named tests

I

Five tests that turn up in every paper.

#	Reaction	Reagents & conditions	What it does	Exam trap
76	Tollens' test	$[Ag(NH_3)_2]^+$ (ammoniacal $AgNO_3$)	Silver mirror with aldehydes	Also HCOOH and α-hydroxy ketones (e.g. fructose); ketones generally don't
77	Fehling's test	Cu^{2+} tartrate complex, alkaline	Red Cu_2O with aliphatic aldehydes	Benzaldehyde does not respond
78	Lucas test	Conc. HCl + anhydrous $ZnCl_2$	Turbidity: 3° at once, 2° in about 5 min, 1° not at room temperature	Based on carbocation stability (SN1)
79	Carbylamine test	1° amine + $CHCl_3$ + alcoholic KOH, heat	Isocyanide (foul smell)	Only 1° amines, aliphatic or aromatic
80	Hinsberg test	$C_6H_5SO_2Cl$ (benzenesulphonyl chloride)	1°: product dissolves in alkali; 2°: insoluble; 3°: no reaction	The 1° sulphonamide has an acidic N–H

QUICK REFERENCE

Carbon-count cheat sheet

ONE CARBON FEWER

Hofmann bromamide · Curtius · Hunsdiecker · Decarboxylation (soda lime) · Iodoform (the acid formed)

ONE CARBON MORE

Arndt–Eistert · Grignard with CO_2 · Nitrile from R–X with KCN, then hydrolysis or reduction

CHAIN DOUBLED

Wurtz · Fittig · Ullmann · Frankland · Kolbe electrolysis

SAME COUNT, NEW GROUP

Rosenmund · Stephen · Clemmensen · Wolff–Kishner · Finkelstein · Swarts

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