

Chem. 118B Workshop/LSC/D. Kent & J. Hollister/Major Reactions Of Aldehydes and Ketones From Ch. 17, Vollhardt & Schore, 4E

Name	Type	Reagents, Catalysts, Solvents, etc.	Product(s)	Comments
1. Addition of Water (Hydration)	Nuc Addition	H ₂ O/H ⁺ cat. or H ₂ O/OH ⁻ cat.	RC(OH) ₂ R' Geminal Diol	geminal diol = carbonyl hydrate. Hydration is reversible: equilibrium lies to left for ketones (K < 10 ⁻²); For aldehydes, about equal (K ~ 1); for Cl ₃ C(O)H, to right, (K > 10 ⁴).
2. Acetal Formation	Nuc Addition/ Elimination/ Nuc Addition	2 ROH/H ⁺	Acetal (+ H ₂ O)	reversible; addition of 1 equivalent of ROH forms hemiacetal; cyclic acetal ("Bart Simpson") used to protect carbonyl group and is stable to base.
3. Raney Nickel Reaction	Reduction (Hydrogenation)	1) HSCH ₂ CH ₂ SH/BF ₃ ; 2) H ₂ /Raney Nickel	Alkane	first step forms cyclic thioacetal which is stable to base & acid; Ra-Ni also reduces C/C double bonds; (H ₂ O, HgCl ₂ , CaCO ₃ , CH ₃ CN hydrolyzes thioacetal back to carbonyl group).
4. Imine Formation	Addition/ Elimination	RNH ₂ /H ⁺ (1 ^o amine)	Imine (+ H ₂ O)	1 ^o amine derivatives (hydrazine, hydroxyl amine, phenylhydrazine, semicarbazides) react by same mechanism.
5. Enamine Formation	Addition/ Elimination	R ₂ NH/H ⁺ (2 ^o amine)	Enamine (+ H ₂ O)	-C=C-NR ₂
6. Wolff-Kishner Reduction	Reduction	NH ₂ NH ₂ /OH ⁻ /H ₂ O/Δ (hydrazine)	Alkane	rigorously basic conditions; complements Clemmensen Reduction (Ch. 16) and Raney Nickel Reaction.
7. Cyanohydrin Formation	Addition	HCN (H ⁺ /KCN)	-C(OH)(C≡N)- Cyanohydrin	useful in synthesis of monosaccharides and amino acids (Chem. 118C)
8. Wittig Reaction	1) S _N 2 2) acid/base 3) addition/	1) PPh ₃ (Ph = phenyl) 2) BuLi (forms ylide) 3) aldehyde or ketone elimination	Alkene	start with methyl, 1 ^o or 2 ^o RX; may get mixture of <u>E</u> and <u>Z</u> alkene products.
9. Baeyer-Villiger Oxidation	Oxidation	RCO ₃ H (peroxycarboxylic acid)	Ester	ketones only; if R groups of ketone are not the same, O from peroxyacid prefers: 3 ^o > cyclohexyl > 2 ^o ~ benzene > 1 ^o > -CH ₃
10. Qualitative Tests for Aldehydes	Oxidation	a) Cu ²⁺ /OH ⁻ (Fehling's Test) b) Ag ⁺ /NH ₃ (Tollen's Test)	Cu ₂ O _(s) (red ppt.) Ag _(s) (silver mirror)	organic product = carboxylate anion from oxidation of aldehyde; NR with other organic compounds.