REACTIVITY OF VARIOUS NUCLEOPHILES and REDUCING AGENTS

In the table below, + means reaction and -- no reaction; blanks are uncertain. Also given are the name of the reaction, the site of reaction (if ambiguous) and the catalyst of choice (in parentheses). You might wish to mark the reactions we have studied as you review. The site of reactions of α,β-unsaturated aldehydes, ketones and esters is susceptible to steric hindrance; the data given is for unhindered compounds. Strong bases (like acetylide and even Grignard) can react not just at the carbonyl but can remove the α-H in an acid-base reaction.

functional group > reacts with this nucleophile	aldehyde	ketone	ester	α,β-unsat ald, ket, or ester	acid chloride	alkyl halide
aldehyde or ketone enolate	+ aldol (OH-)	+ aldol (OH-)	+ (OR-)	+, β-C (OR-)	+	+, S_N2 (LDA)
ester enolate	+ (OR-)	+ (OR-)	+ Claisen (OR-)	+, β-C (OR-)	+	+, S_N2 (OR-)
malonate acetoacetate, etc	+ (OR- or R_2NH)	+ (OR- or R_2NH)	+	+, β-C (OR- or R_2NH)	+	+, S_N2 (OR-)
enamine or lithium enolate	slow	slow	--	+, β-C	+ –>ketone	+, S_N2
CHR = $P\Phi_3$ Wittig reagent	+	+	+, 1 or 2 moles	+, C = O	+, 1 or 2 moles	slow
RMgX Grignard reagent	+	+	+ 2 moles	+, C = O	+ 2 moles	+ if less ether
R_2CuLi	--	--	--	+, β-C	+ 1 mole	
R_2Cd	--	--	--	--	+ 1 mole	--
RCC-, acetylide	+, α-H	+, α-H		+, β-C		+, S_N2
CN-	+	+	+	+, β-C		+, S_N2
$LiAlH_4$	+	+	+	+, C=O	+	+
$NaBH_4$	+	+	--	+, C=O	+	
OH-	+, diol unstable	+, diol unstable	+ hydrolyze	+, β-C reversible	+ hydrolyze	+, S_N2
H_2/Pt	+	+	--	+, C = C	+	--