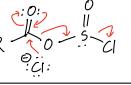
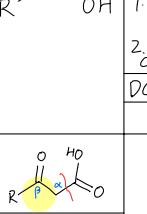
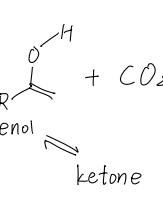
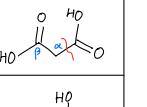
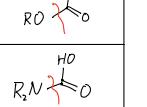
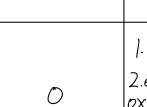
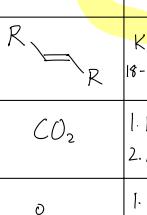
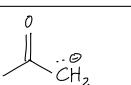
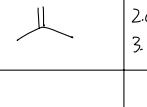


reactant	reagent	product	selectivity	mechanism	intermediate	$C^\oplus$ shift?	comments
$\text{C}=\text{C}$	$\text{H}_3\text{O}^+$	$\text{C}-\text{OH}$	Markovnikov		$\text{C}^\oplus$	✓	
$\text{C}=\text{C}$	$\text{HX}$	$\text{C}-\text{X}$		~	$\text{C}^\oplus$	✓	
$\text{C}\equiv\text{C}$	(excess)	$\text{X}-\text{C}=\text{C}$		trans?	cyclic	X	hard to stop
$\text{C}\equiv\text{C}$		$\text{X}-\text{C}-\text{X}$		~	$\text{cyclic} \rightarrow \text{C}^\oplus$	?	Geminal
$\text{C}=\text{C}$	$\text{H}_2$	$\text{C}-\text{C}$		syn	attach to metal	X	
$\text{C}\equiv\text{C}$	Pd/C	$\text{C}-\text{C}$				X	
$\text{C}\equiv\text{C}$	Pd/CaCO <sub>3</sub> /Pb (Lindlar)	$\text{C}-\text{C}$		cis		X	
$\text{C}\equiv\text{C}$	$\text{Na}/\text{NH}_3$	$\text{C}-\text{C}$		trans	solvated $e^- \rightarrow$ radical anion $\rightarrow$ weaken $\text{C}\equiv\text{C}$	X	trans $\text{H}-\text{C}-\text{C}$ more stable
$\text{C}=\text{C}$	$\text{X}_2$	$\text{C}-\text{X}-\text{X}$	anti	cyclic			Vicinal
$\text{C}\equiv\text{C}$	Nu:	$\text{C}-\text{Nu}-\text{X}$			breaks weaker bond	X	
$\text{C}\equiv\text{C}$	(excess)	$\text{X}-\text{C}-\text{X}$			?	X	not as favored
$\text{C}=\text{C}$	1. $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$	$\text{C}-\text{OH}$	Markovnikov	anti	cyclic	X	
$\text{C}\equiv\text{C}$	2. $\text{NaBH}_4$	$\text{C}-\text{OH} \rightleftharpoons \text{C}-\text{H}$		(trans)		X	tautomerization
$\text{C}=\text{C}$	1. $\text{BH}_3$	$\text{C}-\text{OH}$	anti-Markovikov	syn	concerted partial bonds	X	
$\text{C}\equiv\text{C}$	2. $\text{H}_2\text{O}_2/\text{OH}^-$	$\text{C}-\text{OH} \rightleftharpoons \text{C}-\text{H}$		(trans/syn)		X	tautomerization
$\text{C}=\text{C}$	1. $\text{O}_3$ 2. $\text{Zn}/\text{H}_2\text{O}$ or $(\text{CH}_3)_2\text{S}$ or $\text{H}_2/\text{Pd}$ (red)	$\text{C}(=\text{O}) + \text{H}-\text{C}(=\text{O})-\text{H}$			cyclic		aldehyde
$\text{C}\equiv\text{C}$	2. $\text{H}_2\text{O}_2$ (oxi.)	$\text{C}(=\text{O}) + \text{HO}-\text{C}(=\text{O})-\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$					carboxylic acid
$\text{C}\equiv\text{C}$	2. ~ (oxi or red)	$\text{C}(=\text{O}) + \text{HO}-\text{C}(=\text{O})-\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$					always carboxylic acid
$\text{C}=\text{C}$	$\text{R}^\oplus-\text{N}=\text{N}^\ominus$	$\text{R}-\text{N}(\text{R})-\text{N}=\text{N}^\ominus$				X	work for all 1,3-dipole
$\text{C}=\text{C}$	1. $\text{KMnO}_4$ 2. $\text{H}_2\text{O}/\text{OH}^-$	$\text{HO}-\text{C}(=\text{O})-\text{OH}$		syn	similar to 1,3-dipole	X	
$\text{C}=\text{C}$	1. $\text{OsO}_4$ 2. $\text{H}_2\text{O}/\text{Na}_2\text{SO}_3$	$\text{HO}-\text{C}(=\text{O})-\text{OH}$					
$\text{C}=\text{C}$	$\text{CH}_2\text{N}_2 \text{ hv}(\Delta)$	$\text{C}=\text{C}$	add to more sub.		carbene : $\text{CH}_2$ (or $\text{X}_2$ )	X	
$\text{C}=\text{C}$	$\text{CHX}_3 \text{ KOCC(CH}_3)_3$	$\text{C}=\text{C}$				X	
$\text{C}=\text{C}$	$\text{CF}_3\text{CO}_2\text{H}$ (or mCPBA)	$\text{O}$		syn	last O added rest becomes carboxylic acid	X	
$\text{C}=\text{C}$	H Nu   $\text{H}_3\text{N}^\oplus$ :Nu $^\ominus$	$\text{C}-\text{OH}$		anti	prot. $\rightarrow$ S <sub>N</sub> 2-like $\rightarrow$ deprot. S <sub>N</sub> 2 $\rightarrow$ prot.	X	better resonance
$\text{C}=\text{C}$		$\text{HO}-\text{C}-\text{Nu}$		anti-Markovnikov			less hindrance
$\text{C}=\text{C}$	1. $\text{RMgX}$ ether 2. $\text{H}_2\text{O}$	$\text{HO}-\text{C}-\text{R}$		syn	Mg add	X	less hindrance
$\text{C}=\text{C}$	1. $\text{RCu}(\text{CN})\text{Li}_2$ 2. $\text{H}_2\text{O}$	$\text{R}-\text{C}-\text{H}$					R-Li also good
$\text{C}=\text{C}$	1. $\text{LiAlH}_4$ ether 2. $\text{H}_2\text{O}$	$\text{HO}-\text{C}-\text{H}$		anti			good for $\text{C}=\text{O}$
$\text{C}=\text{C}$							

reactant	reagent	product	selectivity (o/m/p)	mechanism	intermediate	$C^{\oplus}$ shift?	comments
							inefficient
		$H_3C\cdot + \text{Br}-\text{CH}_2-\text{CH}_2-\text{Br}$					
	H-Br $\xrightarrow[70^\circ]{hv}$		anti-Markovnikov		$C\cdot$	✓	Br only
	H-Br $\xrightarrow[70^\circ]{hv}$ (excess)		anti-Markovnikov		vinyl $C\cdot$		
			anti-M x2		$C\cdot$		vicinal
	$CX_4 \xrightarrow[70^\circ]{hv}$		anti-M ?		$C\cdot$	X	$X = Cl, Br$
	$X_2$ (dilute) $\xrightarrow{hv}$		mostly more subbed (~M)		$C\cdot$	X	Br more selective
	NBS $\xrightarrow{\text{trace HBr}}$		allylic		$C\cdot$	✓	$X_2$ conc. must be low, or will be polar addition
	$KNH_2$ $NH_3$		?				$2 \times E_2$
	1. $KNH_2$ $NH_3$ , 2. $H_2O$		terminal alkyne		$PC=$		$\rightleftharpoons$
	$HX \xrightarrow{-70^\circ}$		Markovnikov	syn	$C^{\oplus}$		
	$X_2 \xrightarrow{-70^\circ}$		kinetic: 1,2 thermodynamic: 1,4		$\left. \begin{array}{l} C^{\oplus} \\ \text{cyclic} \end{array} \right\}$		$SnI^+$
	$\Delta$		endo preferred	syn	(concerted)	X	diene in s-cis, $\rightleftharpoons$
	$\Delta$						
	1. $KMnO_4$ (or $H_2Cr_2O_7$ ) 2. $H_3O^+/H_2O$						No $3^\circ$ R!
	1. $Na/NH_3$ 2. $H_2O$		$\text{e}^-$ draw $\text{e}^-$ donate		$\cdot \text{C}_6\text{H}_5\text{C}_6\text{H}_5^{\ominus}$ (+ resonance)		
	$H_2 /$ Rh (or Pt oxides) $\text{CH}_3\text{CH}_2\text{OH}$ $\Delta$ /pressure						acid group also reduced to OH
	$D_3O^+ D_2O$						Can poly add
	$SO_3$ $H_2SO_4$		(m)				
	$HNO_3$ $H_2SO_4$ $NO_2^{\oplus}BF_4^-$ $-20^\circ C$		(m)				
	$X_2$ $FeX_3$		(o/p)		$X - X^{\oplus} - FeX_3^{\ominus}$		
	$R-X$ $AlX_3$		(o/p)		$C^{\oplus}$ for $2^\circ, 3^\circ$ $R-X-AlX_3^{\oplus}$ for $1^\circ, Me$ partial bonds	✓	
	$Cl-C(=O)R$ $AlCl_3$		(m)		$R-\overset{\delta^+}{C}(=O)-\overset{\delta^-}{Cl} \cdots AlCl_3 \leftrightarrow$ $AlCl_4^- + R-\overset{\delta^+}{C}(=O)\overset{\delta^-}{O}$	X	$AlCl_3$ used to hydrolyze, not only catalyst $\rightarrow Al(OH)_3$

reactant	reagent	product	selectivity current preferred site (top/bottom)	mechanism	intermediate	$C^\oplus$ shift?	comments
	Zn(Hg)/HCl EtOH  H <sub>2</sub> N-NH <sub>2</sub> KOH HO~O~OH		(o/p)				remove O
			+SO <sub>2</sub> +HCl				
	H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup> Δ						
	H <sub>2</sub> /Pd/C EtOH  1. Sn/HCl 2. OH/H <sub>2</sub> O		(o/p)				
	NaONO HCl		Lots of carbonyl :ll	2HONO → ONONO			
	CF <sub>3</sub> CO <sub>2</sub> H		(m)				
	CuX						X = Cl, Br, CN
	KI						
	HBF <sub>4</sub>						
	H <sub>2</sub> O H <sub>2</sub> SO <sub>4</sub> /Δ						
	H <sub>3</sub> PO <sub>2</sub>						
	E <sup>⊕</sup>		3	SEAr			Slower than benzene 3° favored since no + on N
	E <sup>⊕</sup>		2	SEAr			Faster than benzene more C share + w/A (:A = :NH, :O, :S)
	:Nu <sup>⊖</sup>		NO <sub>2</sub> on o/p				At least one NO <sub>2</sub>
	HNu		2/4				ipso attack
	1. KNH <sub>2</sub> 2. H <sub>2</sub> O		+H <sub>2</sub> ↑ 2 (intra H-bond)				1. loss of H <sup>⊕</sup> Also R-Li → R adds to 2-
	KNH <sub>2</sub> NH <sub>3</sub>						
	H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup> or OH <sup>-</sup>						$\xrightarrow{\text{H}_2\text{O}}$ gem-diol
	ROH ROH <sup>+</sup> or RO <sup>-</sup>						Hemiacetal Not isolable, except for ring
	1. NaCN 2. H <sub>3</sub> O <sup>+</sup>						Acetal Protect C=O from base $\xrightarrow{\text{excess ROH}}$ $\xrightarrow{\text{excess H}_2\text{O}}$
	1. NaHSO <sub>3</sub> 2. H <sub>3</sub> O <sup>+</sup>						
	RNH <sub>2</sub> H <sub>3</sub> O <sup>+</sup>		[1°]				imine
	R <sub>2</sub> NH H <sub>3</sub> O <sup>+</sup>		[2°] (3° no rxn)	add → E2			enamine (less stable)
	1. R-Li (R-MgX) 2. H <sub>3</sub> O <sup>+</sup>						H <sub>2</sub> O destroys organometallic. Needs to apply separately
	LiAlH <sub>4</sub>						In reversible
	NaBH <sub>4</sub>						
	(Ph) <sub>3</sub> P=CR <sub>2</sub>				$(\text{Ph})_3\text{P}^+ - \text{CH}_2 \rightarrow (\text{Ph})_3\text{P}-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2$ (oxophosphetane)		Wittig rxn Reverse of ozonolysis

reactant	reagent	product	selectivity [#°]	mechanism	intermediate	C <sup>+</sup> shift?	comments
$R-C-OH$	$Na_2CrO_4$ $(Na_2Cr_2O_7)$ $H_3O^+$	$R-C(=O)OH$					$2^\circ OH \rightarrow \text{ketone}$ $1^\circ OH \rightarrow \text{aldehyde} \rightarrow \text{acid}$
	$HNO_3$		[1~2°]		$R-C(=O)OH \xrightarrow{HO} R-C(OH)_2$		
	$KMnO_4$		[1°]				$[O] \text{ also } = RuO_4$
	$CrO_3$ pyridine lit careful, :)		[1-2°]	add → E2	$R-C(H)-O-Cr=\overset{\overset{OH}{  }}{O} \xrightarrow{E2}$		further oxidize to acid (?)
	PCC	$R-C(=O)H$	[1-2°]				No $\sim_2 O$ in reagent, so aldehyde can't hydrate
	$MnO_2$		[allylic/benzylic]				
	$DMSO[\text{;}s=0]/$ $CICOOCOCl/$ $:NET_3$	$R-C(=O)H$	[1-2°]	intramolecular E2	$\begin{array}{c} Cl \\   \\ S^+ \end{array}$		
	$CH_2=CH_2$				$\begin{array}{c} Cl \\   \\ S^+ \end{array}$		OH protecting group
	$R-O-Si-CH_3$	$R-O-Si-CH_3$			$\begin{array}{c} Cl \\   \\ S^+ \end{array}$		
	$H_2O$ $H_3O^+$	$R-OH$					Regenerate OH
$R-SH$	$H_2O$ $H_3O^+$	$R-OH$					
	$HNO_3$	$R-S(=O)OH$					$S$ gets oxidized, not $C$ , as in alcohol
$R-S-R$	$Br_2$ (or $I_2$ ) base	$R-S-S-R$		$S_N2$	$R-S^- \rightarrow R-S-Br$		$KHCO_3$ deprots $RS-H$ .
	$ROOH$ (excess)	$R-S(=O)R$			$R-S(=O)R$		$RSOR/RSO_2R$ tetrahedral $-O-\overset{\overset{S}{ }}{S}-O^-$ preferred
$2R-Li$	$CuBr$	$R_2CuLi$					
$R-X$	$R_2CuLi$	$R-R'$ $+ R'-Cu + Li-X$	[ $R$ is $1^\circ/2^\circ$ ]		$R:\Theta$		$R-Li, R-MgX$ strong $B:\Theta$ , not $Nu:\Theta$
	$LiAlH_4$ $LiHB(Et)_3$	$R-H$		$S_N2?$	$H:\Theta$		
$R-COOH$	$1.2R'-Li$ $2. H_2O$	$R-C(=O)R'$			$R-C(=O)R' \xrightarrow{H_2O} R-C(OH)R'$ hydrate $R'$		acid deprot. first. Then $R'-Li$ add Dianion has no good LG → must ketone
	$1. LiAlH_4$ $2. H_2O$	$R-C(=O)OH$		add → elim	$R-C(=O)OH \xrightarrow{LiAlH_4} R-C(=O)R' \xrightarrow{LiAlH_4} R-C(=O)R'$		Aldehyde as intermediate, but will reduce again. $LiAlH_4$ is a good LG
	excess $R'OH$ $R'DH_2$	$R-C(=O)OR'$		add → elim	$R-C(=O)OR' \xrightarrow{H_2O} R-C(OH)OR'$		ana. hemiacetal can poly can be intra (lactone)
	1. $NaOH$ 2. $R'-LG$						
	$CH_2N_2$	$R-C(=O)OCH_3$	methyl ester only	$S_N2$	$R-C(=O)OCH_3 + H_3C-N\equiv N:$		
$R-COOH$	$R'NH_2$ intense $\Delta$ $DCC$	$R-C(=O)NR'R'$			$R-C(=O)O^- + H_3NR$ ammonium salt		intense heat
				add → elim.	$R-C(=O)NR'R' + H_3N^+$		Change LG ( $OH$ ) can poly can be intra (lactam)

reactant	reagent	product	preference	mechanism	intermediate	$C^\oplus$ shift?	comments	
$R-C(=O)OH$	$SOCl_2$	$R-C(=O)Cl$		add $\rightarrow$ elim			ana. $R-OH \xrightarrow{SOCl_2} R-Cl$	
	$PCl_5$							
	1. $NaOH$ 2. $Cl-CH_2-CH_2-Cl$	$R-C(=O)-O-C(=O)R'$		add $\rightarrow$ elim			(dehydrating reagents) cyclic anhydride	
	DCC ( $CoP_2O_5$ ) $\Delta$ (melt)							
		$R-C(=O) + CO_2$	$\Delta$	intramolecular Diels-Alder-like			$\beta$ -keto acid $\rightarrow$ ketone	
		$HO-C(=O)+CO_2$					malonic acid $\rightarrow$ acid	
		$ROH + CO_2$					monoester of c. acid $\rightarrow$ alcohol diester stable, since no H to lose	
		$R_2NH + CO_2$					$N-NH_2$ OR stable, also no H	
$R-C(=O)OH$	1. $NaOH$ 2. electrochemical oxidation	$R-R + CO_2$		radical	$R-C(=O) \cdot \rightarrow R\cdot$		Kolbe electrolysis	
	1. $Ag_2O$ 2. $Br_2$ , $\Delta$	$R-Br$			$R-C(=O)Br \rightarrow R\cdot + CO_2$		Hunsdiecker rxn. Chain	
	1. $I_2$ (or $Br_2$ ) 2. $H_3O^+$ $H_2O$	$R-C(=O)OH$	Methyl ketone only	add $\rightarrow$ elim	$R-C(=O)Cl \rightarrow C_3I_3^-$ (stable)		Haloform rxn I makes H more acidic	
$R-C(=O)CH_3$	$NaOH$							
$R-C(=O)R$	$KMnO_4 /$ 18-Crown-6/ $H_3O^+$						Like ozonolysis	
$CO_2$	1. $R-MgBr$ 2. $H_3O^+$ $H_2O$			add elim				
	1. LDA 2. $CO_2$ 3. $H_3O^+$ $H_2O$	$\text{R}-C(=O)-CO_2H$						
$R-C(=O)X$	$Nu^\ominus$	$R-C(=O)-Nu$					$Nu^\ominus = H_2O, HOR, NHR,$ $N_3^\ominus, CN^\ominus, RCOO^\ominus, CH_3N_3^\ominus$	
	1. $LiAlH_4$ 2. $H_2O$	$R-C(H_2)-OH$		add/elim $\rightarrow$ add	$R-C(H)-H$			
	1. $2R'MgBr$ 2. $H_2O$	$R-C(OH)-R'$			$R-C(R)-R'$		2 e.g.	
$R-C(=O)X$	1. $LiAl(OCl(C_2H_5)_2)_2H$ 2. $H_2O$	$R-C(=O)-H$	aldehyde	add elim			bulky	
	$H_2 /$ Pd/Quinoline/5						Rosenmund reduction deactivated catalyst	
	1. $R'CuLi$ 2. $H_2O$	$R-C(R)-R'$						
$R-C(=O)OR'$	$Nu^\ominus$	$R-C(=O)-Nu$		add elim				
	$\text{O}_2 / AlCl_3$				$R-C(=O)^+ + Cl_3Al-O-C(=O)R$		F. C.	

reactant	reagent	product	preference	mechanism	intermediate	$C^\oplus$ shift?	comments
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$	$\text{H}_2\text{O}$ (or $\text{OH}^-$ )	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array}$		add elim add			ester hydrolysis
	$\text{HOR}''$ (or $\text{OR}''$ )	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OR}'' \end{array}$					transesterification
	further $\text{HOR}''$ $\text{H}_2\text{OR}''$	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OR}'' \\   \\ \text{R}-\text{C}-\text{OR}'' \end{array}$					ortho ester unstable. acetal/ketone / o.e. no resonance, but ester has
	$1. 2\text{R}'\text{MgBr}$ $2. \text{H}_2\text{O}$	$\begin{array}{c} \text{OH} \\   \\ \text{R}-\text{C}-\text{R}' \end{array}$			$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{R}' \end{array}$		2 eq.
	$1. \text{LiAlH}_4$ (or $\text{NaBH}_4$ ) $2. \text{H}_2\text{O}$	$\text{R}-\text{CH}_2-\text{OH} + \text{HOR}$		add/elim → add	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{H} \end{array}$		$\text{NaBH}_4$ won't work
	$1. \text{DIBAL-H}$ $2. \text{H}_2\text{O}$	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{H} \end{array}$			DIBAL-H =		
	$\text{NH}_3$ (or $\text{NH}_4^+$ )	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$		add elim			
	$1. 3\text{R}'\text{MgBr}$ $2. \text{H}_2\text{O}$	$\begin{array}{c} \text{OH} \\   \\ \text{R}-\text{C}-\text{R}' \end{array}$		3 eq.			
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$	$\text{H}_2\text{O}$ $\text{H}_2\text{SO}_4$	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array}$		add elim	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array} + \text{NH}_2 \rightarrow \text{salt}$		slow, but irreversible
	$1. \text{LiAlH}_4$ $2. \text{H}_2\text{O}$	$\text{R}-\text{CH}_2-\text{NH}_2$		add/elim → weird stuff	$\begin{array}{c} \text{O}-\text{AlH}_2 \\   \\ \text{R}-\text{C}-\text{NH}_2 \\   \\ \text{H} \end{array} \rightarrow \begin{array}{c} \text{H}^\oplus \\   \\ \text{R}-\text{C}-\text{NH}_2^\oplus \end{array}$ iminium ion		Gets $\text{NH}_2$ , not $\text{OH}^-$ ! $\text{NaBH}_4$ won't work
	$\text{P}_2\text{O}_5$ $\Delta$	$\text{R}-\text{C}\equiv\text{N}$		dehydration			
	$\text{Nu}^\ominus$	$\begin{array}{c} \text{R} > \text{C}=\ddot{\text{N}}\text{H} \\ \text{Nu} \end{array}$		add			
$\text{R}-\text{C}\equiv\text{N}$	$\text{H}_2\text{O}$ (or $\text{OH}^-$ )	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array}$		add/elim X3	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH} \end{array} \rightarrow \begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \end{array} \rightarrow \text{amide}$		Stop at ketone Imine has no LG, so survives till $\text{H}_2\text{O}$
	$1. \text{R}'\text{MgBr}$ $2. \text{H}_2\text{O}$	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{R}' \end{array}$		add/elim → hydrolysis	$\begin{array}{c} \text{R}'^\oplus \\   \\ \text{R}-\text{C}-\text{NH} \\   \\ \text{H} \end{array} \xrightarrow{\text{H}_2\text{O}} \text{imine}$		
	$1. \text{LiAlH}_4$ $2. \text{H}_2\text{O}$	$\text{R}-\text{CH}_2-\text{NH}_2$					
	$\text{H}_2$ / Raney Ni	$\text{R}-\text{CH}_2-\text{NH}_2$		$1^\circ$ amine less reactive than $=$			
$\text{R}_2\text{C}=\text{C}=\text{O}$	$\text{Nu}^\ominus$	$\begin{array}{c} \text{O} \\    \\ \text{R}_2\text{C}-\text{NH}_2 \end{array}$			$\left[ \text{R}_2\text{C}=\text{C}^\ominus \leftrightarrow \text{R}_2\text{C}-\text{NH}_2 \right]$ enolate		sp C very reactive
$\text{R}-\text{C}(=\text{O})-\text{R}$	$\text{RCO}_3\text{H}$	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{R} \end{array}$	$\text{H} > 3^\circ > 2^\circ > 1^\circ > 0^\circ$			X	Baeyer-Villiger
$\begin{array}{c} \text{N}-\text{OH} \\    \\ \text{R}-\text{C}-\text{R} \end{array}$ oxime	$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}-\text{R} \end{array}$ amide		backside attack	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}-\text{R} \end{array} \xrightarrow{\text{H}_2\text{O}} \left[ \begin{array}{c} \text{R}^\oplus \\   \\ \text{N}^\ominus \end{array} \leftrightarrow \begin{array}{c} \text{R}^\oplus \\   \\ \text{N}^\ominus \end{array} \right] \xrightarrow{\text{H}_2\text{O}}$		Beckman
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{Cl} \end{array}$	$: \text{NR}_3$	$\text{R}-\text{C}=\text{C}=\text{O}$ $(3^\circ \text{N})$			$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}-\text{R} \end{array} \xrightarrow{\text{H}_2\text{O}} \left[ \begin{array}{c} \text{R}^\oplus \\   \\ \text{N}^\ominus \end{array} \leftrightarrow \begin{array}{c} \text{R}^\oplus \\   \\ \text{N}^\ominus \end{array} \right] \xrightarrow{\text{H}_2\text{O}}$	X	Wolff carbene can add to $=$ or insert between $\text{C}-\text{H}$ Arndt-Eistert rxn: adds a C to R $\text{RCO}_2\text{H} \rightarrow 1. \text{SOCl}_2, 2. \text{CH}_2\text{N}_2, 3. \Delta/\text{Ag}, 4. \text{H}_2\text{O}$ Curtius migration when lose $\text{N}_2$
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{N}^\ominus-\text{N}^\oplus=\text{N}: \end{array}$	$\text{h}\nu/\Delta/\text{Ag}$	$\text{R}-\text{C}=\text{C}=\text{O}$ ketene					
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{N}^\ominus-\text{N}^\oplus=\text{N}: \end{array}$	$\text{h}\nu/\Delta$	$\text{O}=\text{C}=\ddot{\text{N}}-\text{R}$ isocyanate					
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}(=\text{O})-\text{NH}_2 \end{array}$	$1. \text{Br}_2$ $2. \text{H}_2\text{O}/\text{KOH}$	$\text{R}-\text{NH}_2$ $+ \text{CO}_2 + \text{H}_2\text{O}$			$\begin{array}{c} \text{Br} \\   \\ \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \\   \\ \text{Br} \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \\   \\ \text{HO} \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \\   \\ \text{HO} \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}_2 \\   \\ \text{HO} \end{array} \xrightarrow{\text{H}_2\text{O}}$ isocyanate carbamic acid decarboxylation	X	Hofmann isocyanate not isolable -   C
$\text{O}=\text{C}=\ddot{\text{N}}-\text{R}$	$\text{Nu}^\ominus$	$\begin{array}{c} \text{O} \\    \\ \text{Nu}-\text{C}-\text{NH}-\text{R} \end{array}$					Very reactive

reactant	reagent	product	preference	mechanism	intermediate	$C^\oplus$ shift?	comments
<p>(or RO)</p>	$D_2O$ (or $OD^-$ )						Also racemization
	$X_2$						Stops at mono
	$-OH$						All the way. If $CH_3 \rightarrow$ haloform
	1. LDA 2. $R'-X$		$No \beta^o R$	$S_N2$	enolate)		Works for aldehyde, ketone For acid need 2 eq. LDA, +3. $H_3O^+$
	1. $NaOR$ 2. $R'-X$						Then, 1. $H_3O^+$ , 2. gentle $\Delta \rightarrow -CO_2$ $\rightarrow$ acid or ketone (malonic ester synthesis)
	1. $R'-X$ 2. $H_2O$ $H_3O^+$		$2^o$ amine				Problem: >1 enamine may form
	1. $BuLi$ THF 2. $R-X$ 3. $H_3O^+$ $Mg^{2+}$						$3. RaNi \rightarrow$
	$H_3O^+$			aldehyde ✓ receptor $\rightleftharpoons$ thermo product	enolate $\rightarrow$ add to $C=O$		Aldol
	$OH^-$ or 1. LDA, $78^\circ C$ 2. $X_2$ 3. $H_3O^+$		If LDA, kinetic				Reversible Can be intra LDA stepwise to control enolate
	$RO^\ominus$						Knoevenagel Sometimes Nu: anion not enolate E. $\ominus$
	1. $NaNH_2$ (or LDA) 2. $RO^\ominus$ 3. $H_3O^+$		kinetic, less sub enolate				Claisen Ketone enolate $>$ ester
	1. $NaOR$ 2. $RO^\ominus$ 3. $H_3O^+$						product not favored, but double $\alpha$ deprot. is irreversible until $H_3O^+$ Need leg. $OR^\ominus$ , R's must match
	$Nu^\ominus$						Michael Also can acid-cat. Preferred over $C=O$ add., but not for $Nu^\ominus = LiAlH_4, RMgBr$ yes for $R_2CuLi, RMgBr/cat. CuI$
	1. $NaOEt/HOEt$ 2. $KOH/H_2O$				Michael $\rightarrow$ enolate trans $\rightarrow$ aldol $\rightarrow -H_2O$		
	$Br_2 / PBr_3$			last $S_N2$	acid $PBr_3 \xrightarrow{-} \alpha$ . bromide $\rightleftharpoons$ enol $\xrightarrow{Br_2} \alpha$ -bromo $\alpha$ . b.		HVZ rxn $\alpha$ . bromide + $H_2O/HOR/NH_3 \rightleftharpoons$ $\alpha$ -bromo acid $S_N2$ reactive
	1. $SOCl_2$ 2. $NBS$ $HBr$						
	1. $H_2N^\ominus + HN^\oplus$ 2. $NaOH$ $H_2O$			aldol-like			Mannich $\beta$ -amino ketone
	$KOH$ $H_2O$		$No \alpha-H$	$H^\ominus$ trans	$\text{OH}^\ominus \text{add} \rightarrow R-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}=\text{CH}_2 \rightarrow R-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}=\text{CH}_2 \rightarrow$		Cannizzaro
	$AlCl_3$						
	1. $Al(O-CH(R))_3$ 2. $H_2O$		$R'$ no $\alpha$ -H	$H^\ominus$ trans			Al clamp
	$Ph_3CLi$ DME		thermo				warm temp, weak base Also $KH/BEt_3 \rightarrow$

reactant	reagent	product	preference	mechanism	intermediate	$C^\oplus$ shift?	comments
$\begin{array}{c} CHO \\   \\ R \end{array}$	1. NaCN / $H_2O$ 2. $H_2$ / Pd 3. $H_2O$ / $H_3O^+$	$\begin{array}{c} CHO \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array}$			$\begin{array}{c} C\equiv N \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array} \xrightarrow[\text{Pd}]{H_2} \begin{array}{c} H - \text{C} - \text{NH} \\   \\ R \end{array} \xrightarrow[\text{H}_3\text{O}^+]{H_2O}$		Kiliani-Fischer Synthesis + C mix at C(2) poisoned catalyst
$\begin{array}{c} CHO \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array}$	1. $Br_2 / H_2O$ 2. $Ca(OH)_2$ 3. $Fe_2(SO_4)_3 / H_2O / 100^\circ C$ 4. 30% $H_2O_2$	$\begin{array}{c} CHO \\   \\ R \end{array}$	Unknown		$\begin{array}{c} Br_2 / H_2O \\ 2. Ca(OH)_2 \\ \xrightarrow[\text{2. } H_2O_2]{1. Fe_2(SO_4)_3 / H_2O} \begin{array}{c} COO^- \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array} \rightleftharpoons \begin{array}{c} H - \text{C} - \text{O}^- \\   \\ R \end{array} \xrightarrow[\text{2. } H_2O_2]{1. Fe_2(SO_4)_3 / H_2O}$		Ruff degradation
$\begin{array}{c} O = \text{H} \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array}$	$Ca(OH)_2 / H_2O$	$\begin{array}{c} O = \text{H} \\   \\ HO - \text{C} - \text{H} \\   \\ R \end{array} + \begin{array}{c} HO \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array}$		$\rightleftharpoons$	$\begin{array}{c} O \\   \\ HO - \text{C} - \text{H} \\   \\ R \end{array} \rightleftharpoons \begin{array}{c} HO \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array} \xrightleftharpoons{\text{taut.}}$		Lobry de Bruijn-Alberda van Ekenstein
$\begin{array}{c} CHO \\   \\ R \end{array}$	$Br_2 / H_2O$ $0^\circ C$	$\begin{array}{c} CO_2H \\   \\ R \\   \\ CH_2OH \end{array}$ aldonic acid	aldehyde only		$\begin{array}{c} HO \\   \\ R - \text{C} - \text{OH} \end{array} \xrightleftharpoons{Br_2} \begin{array}{c} HO \\   \\ R - \text{C} - \text{Br} \\   \\ OH \end{array} \rightleftharpoons \begin{array}{c} O \\    \\ R - \text{C} - \text{OH} \end{array}$		Mild
$\begin{array}{c} CHO \\   \\ CH_2OH \end{array}$	$NaNO_2 / HNO_3$	$\begin{array}{c} CO_2H \\   \\ R \\   \\ CO_2H \end{array}$ aldaric acid	aldehyde + $1^\circ \text{OH}$				More vigorous Also $\text{CrO}_3$ and $\text{KMnO}_4 / H_3O^+$ Even more: $\text{NaIO}_4$
$\begin{array}{c} CHO \\   \\ R \end{array}$	$3 \text{ PhNH}_2 \text{NH}_2$ $H_3O^+$	$\begin{array}{c} H - \text{C} = N - \text{NHPH} \\   \\ R \end{array}$		enamine	$\begin{array}{c} C = N \text{Ph} \\   \\ H - \text{C} - \text{OH} \\   \\ R \end{array} \rightleftharpoons \begin{array}{c} H - \text{C} - \text{NHPH} \\   \\ R \end{array} \rightleftharpoons \begin{array}{c} HO \\   \\ R - \text{C} - \text{NHPh} \end{array}$ $\text{enamine} + \text{enol}$ $\begin{array}{c} H - \text{C} - \text{NHPH} \\   \\ R - \text{N} - \text{NHPh} \end{array} \rightleftharpoons \begin{array}{c} H - \text{C} - \text{NHPH} \\   \\ R - \text{N} - \text{NHPh} \end{array} = \begin{array}{c} \text{H} \\   \\ \text{N} - \text{NHPh} \\   \\ \text{H} \end{array}$ $\Rightarrow \begin{array}{c} \text{H} \\   \\ \text{N} - \text{NHPh} \end{array} + \text{NH}_2\text{Ph} = \begin{array}{c} M \\   \\ \text{N} - \text{NHPh} \end{array} \xrightarrow{\text{Pb(IV) ox}} \begin{array}{c} \text{H} \\   \\ \text{N} - \text{NHPh} \end{array} = \begin{array}{c} \text{H} \\   \\ \text{N} - \text{NHPh} \end{array} + \text{NH}_3$ $\text{R - dimine exchange}$		Osazone No stereo at C(2)
	$CH_3OH$ / $HCl$		More stable $C^\oplus$ (conomeric)	$SnI$			Acetal (glycoside (pyranoside, furanoside)) Stable under base, no Ether syn. Same for cat. $HCl / H_2O$
$RO - \text{CH}_2\text{Ph}$	$H_2 / Pd$	$R - \text{OH}$					mild, protecting group
	$h\nu$ (or $\Delta$ )		$4n: \Delta \text{ con}, h\nu \text{ dis}$ $4n+2: \Delta \text{ dis}, h\nu \text{ con}$				Electrocyclic rxn
	$h\nu$ (or $\Delta$ )		$4n: \Delta X, h\nu \checkmark$ $4n+2: \Delta \checkmark, h\nu X$	conc.			Cycloaddition
							Sigmatropic rearrangement

# THE END

Glad you've made it this far! The true journey of Orgo has just begun. Stay curious, stay synthesizing, and make your knowledge as boundless as your imagination :))