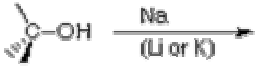
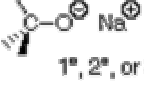
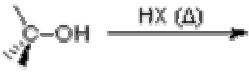





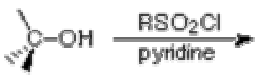
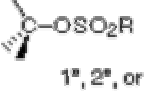
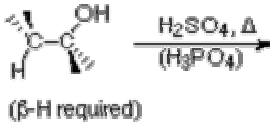

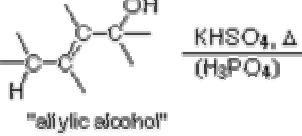
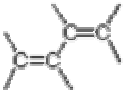

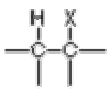

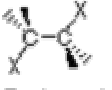

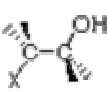

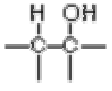
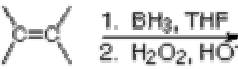



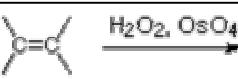




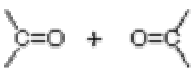





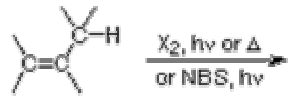
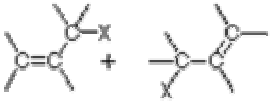
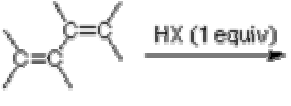
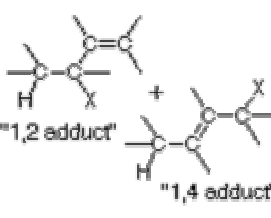
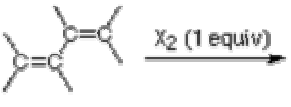
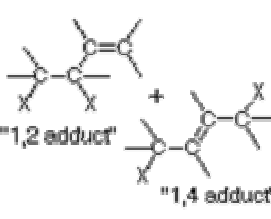
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Reactions of Alcohols - I		
(Carey, Chap. 4 +)		
Reaction	Product	Notes
	 1°, 2°, or 3°	Prep. of alkoxides; conjugate bases of pK _a 16-18 acids
	 X = Cl; 3° only X = Br; 1°, 2° or 3°	S _N 1 subst. (2° & 3°); carbocation intermediate rearrangement possible rel. rates: HBr > HCl; 3° > 2°
	 1°, 2° only	S _N 2 subst.; no rearrangement rel. rates: 1° > 2°
	 1°, 2° only	S _N 2 subst.; no rearrangement rel. rates: 1° > 2°
	 1°, 2°, or 3°	Chap. 8 sulfonate esters good leaving groups, (like halide)
		Chap. 5



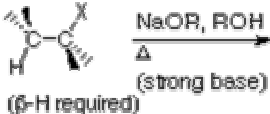

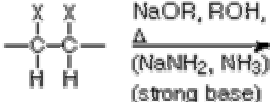
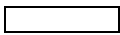
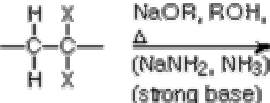
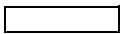
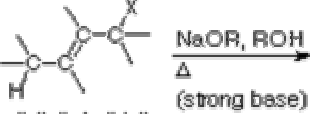
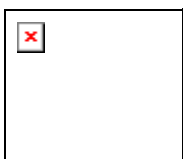
 <p>(β-H required)</p>	 <p>Regio.: Zaitsev's Rule, more subst. alkene (more stable) Stereo.: <i>trans</i>-alkene (more stable)</p>	<p>E1 elimination; carbocation intermediate rearrangement possible</p>
 <p>"allylic alcohol"</p>	 <p>[conjugated diene; most stable]</p>	<p>Chap. 10 allylic carbocation resonance stabilized</p>

Reactions of Alkenes (Carey, Chap. 6 +)		
Reaction	Product	Notes
	 <p>Regio.: "Mark's" Rule (E⁺ = H⁺). Stereo.: n/a</p>	<p>carbocation intermediate rearrangement possible</p>
	 <p>Regio.: n/a Stereo.: <i>anti</i> addition</p>	<p>cyclic halonium ion, no rearrangement Br₂ diagnostic for C=C</p>
	 <p>Regio.: "Mark's" Rule (E⁺ = X⁺) Stereo.: <i>anti</i> addition</p>	<p>cyclic halonium ion, no rearrangement</p>
	 <p>Regio.: "Mark's" Rule (E⁺ = H⁺). Stereo.: n/a</p>	<p>carbocation intermediate rearrangement possible</p>
		<p>synchronous add'n of</p>



	 Regio.: "anti-Mark's" Rule $E^+ = B \rightarrow OH$ Stereo.: <i>syn</i> addition	B & H, no rearrangement
 H_2, Pd (or Pt, Ni, Rh)	 Regio.: n/a Stereo.: <i>syn</i> addition	
 H_2O_2, OsO_4	 Regio.: n/a Stereo.: <i>syn</i> addition	Chap. 15 concerted addition, $6 e^-$ cyclic transition state
 RCO_3H	 Regio.: n/a Stereo.: <i>syn</i> addition	epoxidation; concerted addition
 1. O_3 2. Zn, H_3O^+	 aldehydes and/or ketones	alkene cleavage; useful for structure elucidation
 $KMnO_4, \Delta$	 ketones and/or carboxylic acids (or CO_2)	alkene cleavage; useful for structure elucidation
 mono- or disubst. alkene	$1. X_2, CCl_4$ $2. NaNH_2, NH_3$ $-C \equiv C-$	Chap. 9 addition, followed by double E2 elimination of vicinal dihalide; prep. of alkynes
		Chap. 10

		<p>allylic free radical; resonance-stabilized NBS = <i>N</i>-bromosuccinimide</p>
		<p>Chap. 10 allylic carbocation; resonance-stabilized 1,2-adduct major with "kinetic control" 1,4-adduct major with "thermodyn. control"</p>
		<p>Chap. 10 allylic carbocation; resonance-stabilized 1,2-adduct major with "kinetic control" 1,4-adduct major with "thermodyn. control"</p>

Reactions of Alkyl Halides (Carey, Chap. 8 +)		
Reaction	Product	Notes

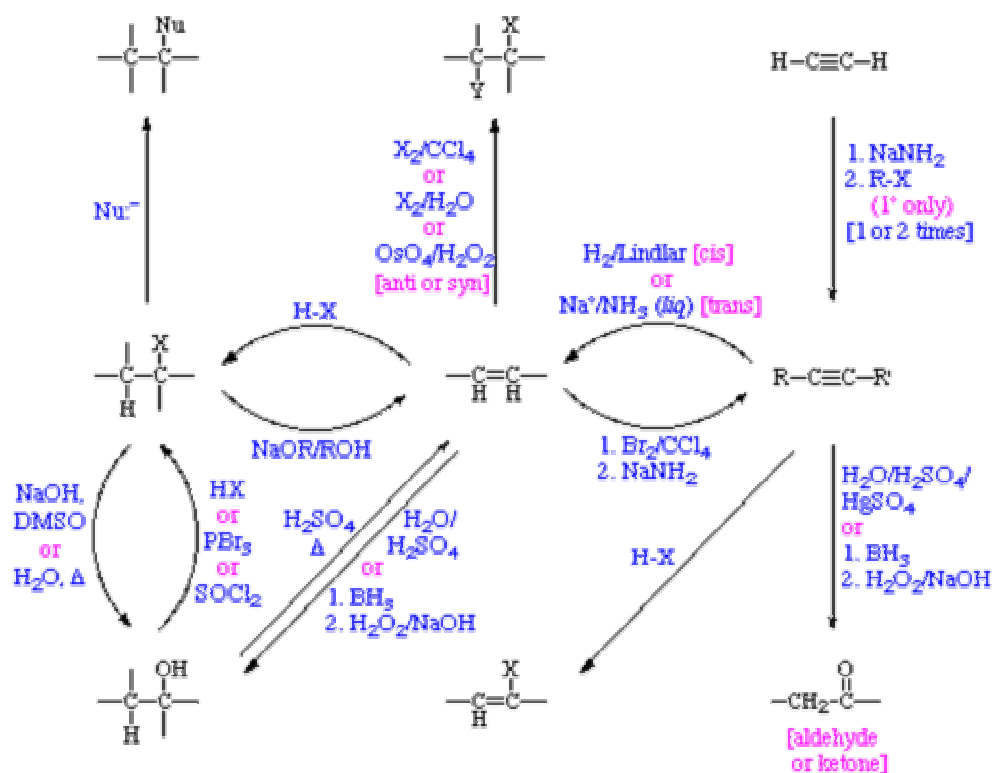
 <p>X = Cl, Br, I, OSO₂R 1°, 2°, or 3°</p>	 <p>1°, always S_N2 2°, S_N2 or S_N1 3°, always S_N1 Stereo.: if S_N2, inversion; if S_N1, racemization</p>	<p>S_N2 with strong Nu:⁻ & polar aprotic solvent.</p> <p>S_N1 with weak Nu: & protic solvent.</p> <p>Rearrangement possible when S_N1.</p>
 <p>(β-H required)</p>	 <p>KO^tBu req. for 1°; any strong base for 2° or 3° Regio.: Zaitsev's Rule, more substituted alkene Stereo.: <i>trans</i> alkene BUT: anti-parallel H & X req. overrides above</p>	<p>also Chap. 5</p> <p>E2 elimination; requires anti-parallel conformation; no rearrangement</p>
 <p>(strong base)</p>		<p>Chap. 9</p> <p>double E2 elimination of vicinal dihalide; prep. of alkynes</p>
 <p>(strong base)</p>		<p>Chap. 9</p> <p>double E2 elimination of geminal dihalide; prep. of alkynes</p>
 <p>"allylic halide"</p>		<p>Chap. 10</p> <p>E1 or E2 elimination</p>





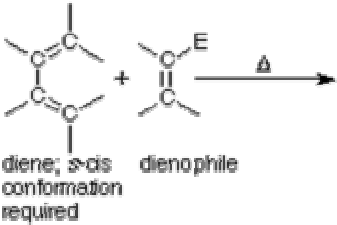
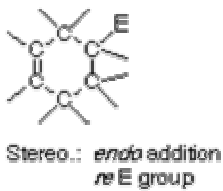
Reactions of Alkynes (Carey, Chap. 9)		
Reaction	Product	Notes
$\text{—C}\equiv\text{C—H} \xrightarrow[2. \text{R-X (1}^\circ \text{ only)}]{1. \text{NaNH}_2}$	$\text{—C}\equiv\text{C—R}$	Prep. of alkynes. NOT for 2° & 3° R-X; get elimination of R-X only
$\text{—C}\equiv\text{C—} \xrightarrow[\text{CHCl}_3]{\text{HX (1 or 2 eq)}}$	$\text{—HC=C} \begin{matrix} \text{X} \\ \diagup \end{matrix}$ or $\begin{matrix} \text{H} & \text{X} \\ & \\ \text{—C} & \text{—C—} \\ & \\ \text{H} & \text{X} \end{matrix}$ (with 1 eq) (with 2 eq) Regio.: "Mark's" Rule (E ⁺ = H ⁺). Stereo.: n/a	
$\text{—C}\equiv\text{C—} \xrightarrow[\text{CCl}_4]{\text{X}_2 \text{ (1 or 2 eq)}}$	$\begin{matrix} \text{X} & \text{X} \\ \diagdown & / \\ \text{C} & = & \text{C} \\ / & \diagdown \\ \text{X} & \end{matrix}$ or $\begin{matrix} \text{X} & \text{X} \\ & \\ \text{—C} & \text{—C—} \\ & \\ \text{X} & \text{X} \end{matrix}$ (with 1 eq) (with 2 eq) Regio.: n/a Stereo.: <i>anti</i> addition	
$\text{H—C}\equiv\text{C—} \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O, H}_2\text{SO}_4}$	$\left[\begin{matrix} \text{OH} \\ \\ \text{H}_2\text{C}=\text{C—} \end{matrix} \right] \rightarrow \text{H}_3\text{C—C(=O)—}$ Regio.: "Mark's" Rule (E ⁺ = H ⁺) Stereo.: n/a	Enol intermediate; methyl ketone from terminal alkyne
$\text{H—C}\equiv\text{C—} \xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-]{1. \text{BH}_3, \text{THF}}$	$\left[\begin{matrix} \text{OH} \\ \\ \text{H—C}=\text{CH—} \end{matrix} \right] \rightarrow \text{H—C(=O)—CH}_2\text{—}$ Regio.: "anti-Mark's" Rule E ⁺ = B (→ OH) Stereo.: n/a	Enol intermediate; aldehyde from terminal alkyne
$\text{—C}\equiv\text{C—} \xrightarrow{\text{H}_2, \text{Lindlar Pd}}$	$\begin{matrix} \text{H} & \text{H} \\ \diagdown & / \\ \text{C} & = & \text{C} \\ / & \diagdown \end{matrix}$ Regio.: n/a Stereo.: <i>syn</i> addition	Synthesis of <i>cis</i> -alkenes










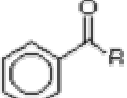
$\text{—C}\equiv\text{C—} \xrightarrow{\text{Na, NH}_3 (\text{liq})}$	 <p>Regio.: n/a Stereo.: <i>anti</i> addition</p>	<p>Synthesis of <i>trans</i>-alkenes</p>
$\text{—C}\equiv\text{C—} \xrightarrow[2. \text{H}_2\text{O}]{1. \text{O}_3}$		<p>Alkyne cleavage; structure elucidation; CO₂ from terminal alkyne</p>

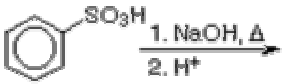
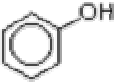


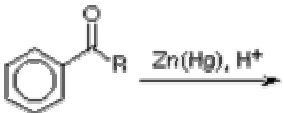
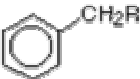
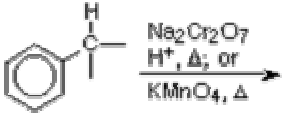
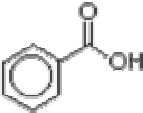
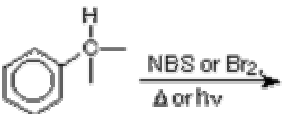
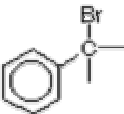
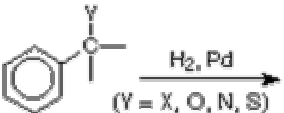
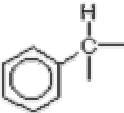
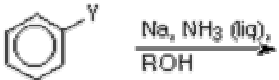
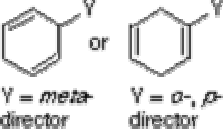
Transformations Flowsheet - Organic I

(Carey, Chap. 4 - 9)





Reactions of Conjugated Dienes (Carey, Chap. 10)		
Reaction	Product	Notes
		allylic carbocation; resonance-stabilized; 1,2-adduct major with "kinetic control" 1,4-adduct major with "thermodyn. control"
		allylic carbocation; resonance-stabilized; 1,2-adduct major with "kinetic control" 1,4-adduct major with "thermodyn. control"
		"Diels-Alder reaction" E must be conjugating group (eg, C=O or C=C); concerted reaction; stereospecific re dienophile

Reactions of Arenes (Carey, Chap. 11 & 12)		
Reaction	Product	Notes
 $\xrightarrow[\text{I}_2, \text{Cu}^{2+}]{\text{X}_2, \text{FeX}_3 \text{ or}}$		
 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3}$		prep. of nitrobenzenes
 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{SO}_3}$		prep. of benzenesulfonic acids
 $\xrightarrow{\text{RCl, AlCl}_3}$		Friedel-Crafts reaction. carbocation intermediate; rearrangement possible; NOT with <i>meta</i> -directors
 $\xrightarrow[\text{AlCl}_3]{\text{RCOCl, AlCl}_3 \text{ or } (\text{RCO})_2\text{O}_1}$		Friedel-Crafts reaction. acyl cation intermediate; no rearrangement; NOT with <i>meta</i> -directors
		Chap. 24.6

		<p>prep. of phenols</p>
		<p>Chap. 22.10</p> <p>prep. of anilines;</p> <p>SnCl₂ selective for NO₂</p>
		<p>Zn selective for aryl C=O</p>
		<p>Must have at least 1 benzylic H;</p> <p>prep. of benzoic acids;</p> <p>structure elucidation</p>
		<p>benzylic H only</p> <p>free-radical reaction</p>
		<p>benzylic Y only</p>
	 <p>Y = <i>meta</i>-director</p> <p>Y = <i>ortho</i>, <i>para</i>-director</p>	<p>Birch reduction</p>

Reactions of Organometallic Compounds (Carey, Chap. 14)		
Reaction	Product	Notes
$\text{R-X} \xrightarrow[\text{[X = Cl, Br, I]}]{\text{Mg, Et}_2\text{O}}$	R-MgX	<p>Prep. of Grignard reagent</p> <p>R=any alkyl, vinyl or aryl</p>
$\text{R-X} \xrightarrow[\text{[X = Cl, Br, I]}]{\text{Li, Et}_2\text{O}}$	R-Li + LiX	<p>Prep. of organolithium</p> <p>R=any alkyl, vinyl or aryl</p>
$\text{R-M} \xrightarrow[\text{[M = Li, MgX]}]{\text{H-A}}$	R-H + M ⁺ A ⁻	<p>Acid-base reaction</p> <p>R-M very strong base</p> <p>Very fast when A = O, N or alkyne C</p>
$\text{R-MgX} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{H}_2\text{C=O}}$	R-CH ₂ OH	<p>Syn. of 1° alcohols</p> <p>1-C chain extension</p>
$\text{R-MgX} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{R}'\text{-}\overset{\text{O}}{\parallel}\text{C-H}}$	$\text{R}-\underset{\text{R}'}{\text{C}}\text{HOH}$	Syn. of 2° alcohols
$\text{R-MgX} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{R}'\text{-}\overset{\text{O}}{\parallel}\text{C-R}''}$	$\text{R}-\underset{\text{R}'}{\overset{\text{R}''}{\text{C}}}\text{OH}$	Syn. of 3° alcohols
$\text{R-MgX} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{R}'\text{-}\overset{\text{O}}{\parallel}\text{C-OR}''}$	$\text{R}-\underset{\text{R}'}{\overset{\text{R}''}{\text{C}}}\text{OH} + \text{HO-R}''$	<p>Syn. of 3° alcohols</p> <p>2 equiv of RMgX needed</p>
	R-CO ₂ H	

$\text{R-MgX} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{CO}_2}$		Syn. of carboxylic acids
$\text{R-MgX} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{H}_2\text{C}=\text{O}-\text{CH-R}'}$	$\text{R-CH}_2-\overset{\text{OH}}{\text{C}}-\text{R}'$	Chap. 15 & 16
$\text{R-Li} \xrightarrow{\text{CuX, Et}_2\text{O}}$	$\text{R}_2\text{CuLi} + \text{LiX}$	Prep. of organocuprate 2 equiv of R-Li needed
$\text{R}_2\text{CuLi} \xrightarrow{\text{R}'\text{-X}}$	$\text{R-R}'$	R' = alkyl, vinyl or aryl "coupling" reaction
$\text{C}=\text{C} \xrightarrow[\text{Et}_2\text{O}]{\text{CH}_2\text{I}_2, \text{Zn(Cu)}}$		Syn. of cyclopropanes stereospecific organozinc intermediate carbenoid reaction
$\text{C}=\text{C} \xrightarrow[\text{[X = Cl or Br]}]{\text{CHX}_3, \text{tBuO}^-\text{K}^+}$		Syn. of cyclopropanes carbene intermediate

Reactions of Alcohols - II

(Carey, Chap. 15)

Reaction	Product	Notes
$\begin{array}{c} \\ \text{---C---OH} \\ \\ \text{[any ROH]} \end{array} \xrightarrow[\text{H}_2\text{SO}_4 \text{ (cat)}]{\text{R}'\text{-C(=O)-OH}}$	$\begin{array}{c} \\ \text{---C---O---C(=O)-R}' \\ \end{array}$	<p>"Fischer esterification"</p> <p>equilibrium reaction</p>
$\begin{array}{c} \\ \text{---C---OH} \\ \\ \text{[any ROH]} \end{array} \xrightarrow[\text{pyridine}]{\text{R}'\text{-C(=O)-Cl}}$	<div style="border: 1px solid black; width: 60px; height: 40px; display: flex; align-items: center; justify-content: center;"> x </div>	
$\begin{array}{c} \\ \text{---C---OH} \\ \\ \text{[any ROH]} \end{array} \xrightarrow[\text{pyridine}]{\text{R}'\text{-C(=O)-O-C(=O)-R}'}$	$\begin{array}{c} \\ \text{---C---O---C(=O)-R}' \\ \end{array}$	
$\begin{array}{c} \\ \text{---C---OH} \\ \end{array} \xrightarrow[\text{H}_2\text{SO}_4 \text{ (cat)}]{\text{HONO}_2}$	$\begin{array}{c} \\ \text{---C---O---NO}_2 \\ \end{array}$	<p>nitrate ester</p>
$\begin{array}{c} \\ \text{---C---OH} \\ \end{array} \xrightarrow{\text{H}_2\text{SO}_4}$	$\begin{array}{c} \\ \text{---C---O---SO}_3\text{H} \\ \end{array}$	<p>hydrogen sulfate ester</p> <p>sulfate diester possible</p>
$\begin{array}{c} \\ \text{---C---OH} \\ \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{H}_3\text{PO}_4}$	$\begin{array}{c} \\ \text{---C---O---P(=O)(OH)}_2 \\ \end{array}$	<p>phosphate ester</p> <p>diester & triester possible</p>
$\begin{array}{c} \text{H} \\ \\ \text{---C---OH} \\ \\ \text{H} \\ \text{[1}^\circ \text{ ROH]} \end{array} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{PCC}}$	$\begin{array}{c} \text{O} \\ \\ \text{---C---H} \end{array}$ <p>aldehyde</p>	<p>"PCC" = pyridinium chlorochromate</p>
$\begin{array}{c} \text{H} \\ \\ \text{---C---OH} \\ \\ \text{H} \\ \text{[1}^\circ \text{ ROH]} \end{array} \xrightarrow[\text{H}_2\text{SO}_4, \text{H}_2\text{O}]{\text{Na}_2\text{Cr}_2\text{O}_7}$	$\begin{array}{c} \text{O} \\ \\ \text{---C---OH} \end{array}$ <p>carboxylic acid</p>	<p>"Jones reagent"</p> <p>oxidant = H₂CrO₄</p>
	$\begin{array}{c} \text{O} \\ \\ \text{---C---} \end{array}$ <p>ketone</p>	

$\begin{array}{c} \text{H} \\ \\ \text{C}-\text{OH} \\ \\ \text{[2}^\circ \text{ ROH]} \end{array} \xrightarrow{\text{PCC or Jones}}$		
$\begin{array}{c} \\ \text{C}-\text{OH} \\ \\ \text{[3}^\circ \text{ ROH]} \end{array} \xrightarrow{\text{PCC or Jones}}$	$\begin{array}{c} \\ \text{C}-\text{OH} \\ \\ \text{no reaction} \end{array}$	
$\begin{array}{c} \text{HO} \quad \text{OH} \\ \quad \\ \text{C}-\text{C} \\ \quad \\ \text{[vicinal diol]} \end{array} \xrightarrow{\text{HIO}_4}$	$\begin{array}{c} \diagdown \quad \diagup \\ \text{C}=\text{O} + \text{O}=\text{C} \\ \diagup \quad \diagdown \\ \text{aldehydes or ketones} \end{array}$	

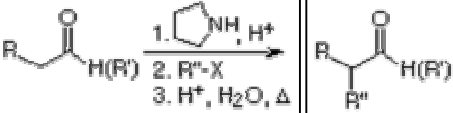
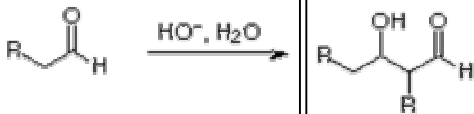
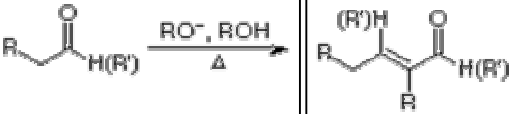
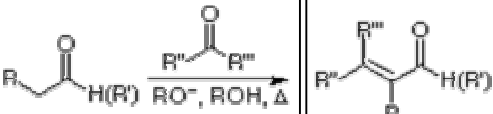
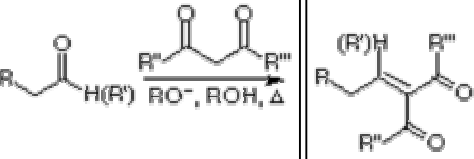
Reactions of Ethers (Carey, Chap. 16)		
Reaction	Product	Notes
$\text{R-O-R}' \xrightarrow[\Delta]{\text{HBr, H}_2\text{O}}$	$\text{R-Br} + \text{R}'\text{-Br}$	ether cleavage
$\begin{array}{c} \text{R}^1 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{R}^2 \quad \text{R}^3 \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{Nu}^-}$ <p style="text-align: center;">[Nu⁻ = strong Nu]</p>	$\begin{array}{c} \text{R}^1 \quad \text{Nu} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{HO} \quad \text{R}^3 \end{array}$ <p style="text-align: center;">Regio.: Nu attack at less-substituted C Stereo.: <i>anti</i> opening</p>	<p style="text-align: center;">S_N2-type opening</p> <p style="text-align: center;">Typical reactants: RO⁻, RMgX, LiAlH₄</p>
$\begin{array}{c} \text{R}^1 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{R}^2 \quad \text{R}^3 \end{array} \xrightarrow{\text{H-Nu, H}^+}$ <p style="text-align: center;">[H-Nu = weak Nu]</p>	$\begin{array}{c} \text{Nu} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{R}^2 \quad \text{OH} \end{array}$ <p style="text-align: center;">Regio.: Nu attack at more-substituted C Stereo.: <i>anti</i> opening</p>	<p style="text-align: center;">acid-catalyzed opening</p> <p style="text-align: center;">S_N1-like reaction</p> <p style="text-align: center;">Typical reactants: ROH/H⁺, RNH₂/H⁺</p>

Reactions of Aldehydes & Ketones		
(Carey, Chap. 17)		
Reaction	Product	Notes
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightleftharpoons{\text{H}_2\text{O}}$	$\begin{array}{c} \text{HO} \quad \text{OH} \\ \quad \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$	Hydrate formation Equilibrium; K usually < 1
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightleftharpoons{\text{R}''\text{OH}}$	$\begin{array}{c} \text{HO} \quad \text{OR}'' \\ \quad \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$	Hemiacetal formation Equilibrium; K usually < 1, except for 5-6 memb cyclic
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightleftharpoons[\text{H}_2\text{O}, \text{H}^+]{\text{R}''\text{OH}, \text{H}^+} \begin{array}{c} \text{R}''\text{O} \quad \text{OR}'' \\ \quad \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$ <p style="text-align: center;">Δ</p>	$\begin{array}{c} \text{R}''\text{O} \quad \text{OR}'' \\ \quad \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$	Acetal formation Reverse reaction, acetal hydrolysis C=O "protecting" group
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow{\text{R}''\text{SH}, \text{H}^+}$	$\begin{array}{c} \text{R}''\text{S} \quad \text{SR}'' \\ \quad \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$	Thioacetal formation
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[2. \text{H}_2, \text{Ni}]{1. \text{R}''\text{SH}, \text{H}^+}$	$\text{R}-\text{CH}_2-\text{H}(\text{R}')$	

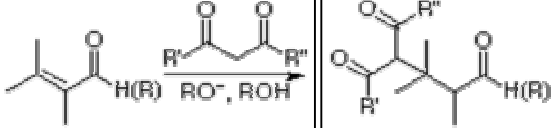
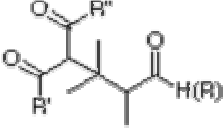
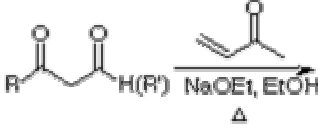
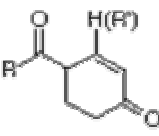
		Thioacetal hydrogenolysis
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow{\text{Y-NH}_2, \text{H}^+} \text{R}-\overset{\text{N}-\text{Y}}{\parallel}{\text{C}}-\text{H}(\text{R}')$	$\text{R}-\overset{\text{N}-\text{Y}}{\parallel}{\text{C}}-\text{H}(\text{R}')$	<p>Y = H or R", imine</p> <p>Y = OH, oxime</p> <p>Y = NH₂ or NHR", hydrazone</p> <p>2,4-DNP diagnostic for alde. or ketone - get orange ppt</p>
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[2. \text{NaBH}_4]{1. \text{R}''\text{NH}_2, \text{H}^+} \text{R}-\overset{\text{R}''\text{NH}}{\text{C}}-\text{H}(\text{R}')$	$\text{R}-\overset{\text{R}''\text{NH}}{\text{C}}-\text{H}(\text{R}')$	Amine synthesis
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[2. \text{HO}^-, \text{DMSO}]{1. \text{NH}_2\text{NH}_2, \text{H}^+} \text{R}-\text{H}(\text{R}')$	$\text{R}-\text{H}(\text{R}')$	"Wolff-Kishner reduction" Decomposition of hydrazone
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[\text{[KCN, H}_2\text{SO}_4]]{\text{HCN}} \text{R}-\overset{\text{HO}}{\text{C}}(\text{C}\equiv\text{N})-\text{H}(\text{R}')$	$\text{R}-\overset{\text{HO}}{\text{C}}(\text{C}\equiv\text{N})-\text{H}(\text{R}')$	Cyanohydrin formation Equilibrium; K > 1 only with alde. or cyclic ketone
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[2. \text{H}_2\text{O, H}^+, \Delta]{1. \text{HCN}} \text{R}-\overset{\text{HO}}{\text{C}}(\text{CO}_2\text{H})-\text{H}(\text{R}')$	$\text{R}-\overset{\text{HO}}{\text{C}}(\text{CO}_2\text{H})-\text{H}(\text{R}')$	Cyanohydrin hydrolysis

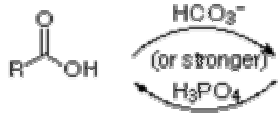

		Carboxylic acid synthesis
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{R}''\text{MgX}}$	$\begin{array}{c} \text{HO} \quad \text{R}'' \\ \quad \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$	Alcohol synthesis
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{NaBH}_4 \text{ or } \text{LiAlH}_4}$	$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{C}-\text{H}(\text{R}') \end{array}$	Prep of 1° or 2° alcohols NaBH ₄ selective for alde. or ketones
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}(\text{R}') \xrightarrow[\text{from: } \begin{array}{l} 1. \text{R}''\text{R}'''\text{CH}_2\text{Br} \\ + \text{Ph}_3\text{P} \\ 2. \text{Et-Li} \end{array}]{\text{Ph}_3\text{P}=\text{CR}''\text{R}'''}{\text{R}''\text{R}'''\text{C}=\text{C}-\text{H}(\text{R}') + \text{PPh}_3}$	$\begin{array}{c} \text{R}'' \quad \text{R}''' \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \\ \text{R} \quad \text{H}(\text{R}') \end{array} + \text{PPh}_3$	"Wittig reaction" Synthesis of alkenes R'' and/or R''' can be H
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \xrightarrow[\text{Ag}^+/\text{HO}^-]{\text{Jones or } \text{Ag}^+/\text{HO}^-}$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	Ag ⁺ /HO ⁻ ("Tollen's reagent") - selective for aldehydes; diagnostic - get silver mirror
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}' \xrightarrow{\text{R}''\text{COOH}}$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	"Baeyer-Villiger oxidation" Cation rearrangement Migratory aptitudes: Ar>3°R>2°R>1°R>CH ₃

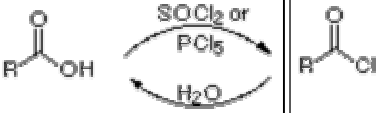
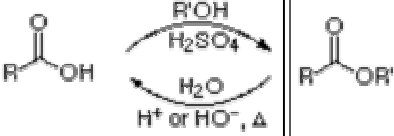

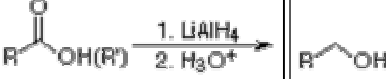
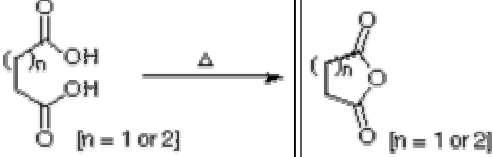
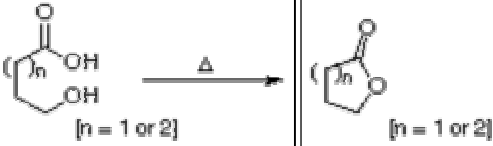

Reactions of Enols, Enolates, Enones		
(Carey, Chap. 18)		
Reaction	Product	Notes
$\text{R}-\text{CH}_2-\text{C}(=\text{O})-\text{H}(\text{R}') \xrightleftharpoons{\text{H}^+ \text{ or } \text{B}^- (\text{cat.})} \text{R}-\text{CH}=\text{C}(\text{OH})-\text{H}(\text{R}')$	$\text{R}-\text{CH}=\text{C}(\text{OH})-\text{H}(\text{R}')$	<p>Keto-enol tautomerism</p> <p>K usually $\ll 1$, but fast</p>
$\text{R}-\text{CH}_2-\text{C}(=\text{O})-\text{H}(\text{R}') \xrightarrow{\text{X}_2, \text{HX} (\text{cat.})} \text{R}-\text{CH}(\text{X})-\text{C}(=\text{O})-\text{H}(\text{R}')$	$\text{R}-\text{CH}(\text{X})-\text{C}(=\text{O})-\text{H}(\text{R}')$	<p>alpha halogenation</p> <p>via enol</p>
$\text{R}-\text{CH}_2-\text{C}(=\text{O})-\text{H}(\text{R}') \xrightarrow[2. \text{R}''-\text{X}]{1. \text{LiN}(\text{iPr})_2} \text{R}-\text{CH}(\text{R}'')-\text{C}(=\text{O})-\text{H}(\text{R}')$	$\text{R}-\text{CH}(\text{R}'')-\text{C}(=\text{O})-\text{H}(\text{R}')$	<p>alpha alkylation;</p> <p>via enolate anion;</p> <p>must use very strong base</p> <p>(to get 100% enolate);</p> <p>R'' must be 1°</p>
$\text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{H}(\text{R}') \xrightarrow[2. \text{R}''-\text{X}]{1. \text{NaOEt}} \text{R}-\text{C}(=\text{O})-\text{CH}(\text{R}'')-\text{C}(=\text{O})-\text{H}(\text{R}')$	$\text{R}-\text{C}(=\text{O})-\text{CH}(\text{R}'')-\text{C}(=\text{O})-\text{H}(\text{R}')$	<p>beta-dicarbonyl</p> <p>alkylation;</p> <p>alkoxide base strong enough;</p> <p>R'' can be 1° or 2°</p>



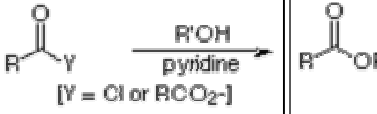
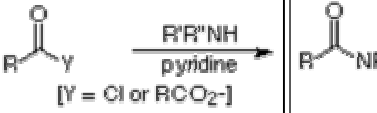


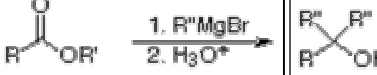
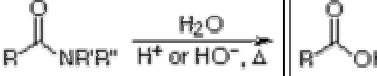
		<p>alpha alkylation via enamine;</p> <p>R''X must be activated halide (benzyl, allyl, alpha to C=O)</p>
		<p>simple aldol condensation;</p> <p>equilibrium;</p> <p>K > 1 for aldehydes only</p>
		<p>aldol with dehydration;</p> <p>prep of conjugated enone works with alde. or ketone</p>
		<p>mixed aldol condensation;</p> <p>R'' & R''' must have no alpha H's</p>
		<p>mixed aldol condensation;</p>

		<p>beta-dicarbonyl cpd</p> <p>gives</p> <p>enolate anion</p> <p>exclusively</p>
		<p>intramolecular aldol;</p> <p>5 or 6 memb. rings only</p>
		<p>1,2-addition major;</p> <p>NaBH₄ gives both 1,2- & 1,4-addition (mixtures)</p>
		<p>1,2-addition major;</p> <p>RMgX gives both 1,2- & 1,4-addition (mixtures)</p>
		<p>conjugate addition (1,4-) only</p>
		<p>conjugate addition (1,4-) only</p>

		<p>Michael reaction</p> <p>(conjugate addition);</p> <p>with beta dicarbonyl enolate</p>
		<p>Robinson annelation:</p> <p>Michael rxn to methyl vinyl ketone,</p> <p>then intramolecular aldol condensation.</p>

<p style="text-align: center;">Reactions of Carboxylic Acids and Derivatives</p> <p style="text-align: center;">(Carey, Chap. 19 & 20)</p>		
Reaction	Product	Notes
		<p>carboxylate anions;</p> <p>water soluble; soaps;</p> <p>HCO₃⁻ diagnostic for carbox.</p> <p>acid (---> CO₂ gas)</p>

		
		<p>Fischer esterification, equilibrium, $K = 1$.</p> <p>Ester hydrolysis, (HO^- cat.= saponification)</p>
		<p>diazomethane; prep. of methyl esters</p>
		<p>reduction of acid or ester to 1° alcohol</p>
		<p>5 or 6 membered ring cyclic anhydride</p>
		<p>5 or 6 membered ring lactone</p>
		

		prep. of anhydrides
		prep. of ketones
		prep. of aldehydes
		prep. of esters
		prep. of amides
		transesterification
		aminolysis of esters
		double addition of Grignard
		hydrolysis of amides; very slow reaction

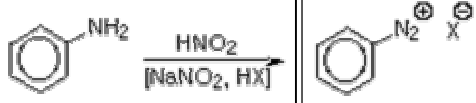
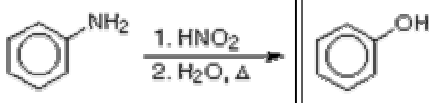
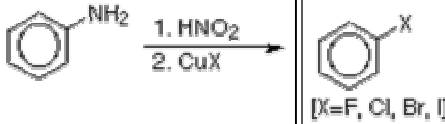
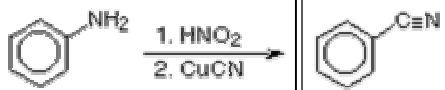
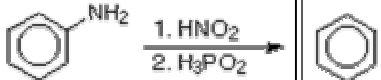
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}'\text{R}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{LiAlH}_4} \text{R}-\text{CH}_2-\text{NR}'\text{R}''$		prep. of amines
$\text{R}-\text{C}\equiv\text{N} \xrightarrow[\Delta]{\text{H}_2\text{O}, \text{H}^+} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$		hydrolysis of nitriles; very slow reaction
$\text{R}-\text{C}\equiv\text{N} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{LiAlH}_4} \text{R}-\text{CH}_2-\text{NH}_2$		prep. of 1° amines
$\text{R}-\text{C}\equiv\text{N} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{R}'\text{MgBr}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$		single addition of Grignard; prep. of ketones
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}(\text{R}')-\text{OH} \xrightarrow[2. \text{H}_2\text{O}]{1. \text{Br}_2, \text{SOCl}_2} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}(\text{Br})(\text{R}')-\text{OH}$		alpha halogenation of carboxylic acids
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \xrightarrow[\text{HO}^-, \text{H}_2\text{O}]{\text{Br}_2} \text{R}-\text{NH}_2$		Hofmann rearrangement; prep. of 1° amines

Ester Condensations (Carey, Chap. 21)		
Reaction	Product	Notes
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{OR}' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{R}'\text{O}^-, \text{R}'\text{OH}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}(\text{R})-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$		Claisen condensation. Must be able to form beta-

		<p>ketoester enolate anion intermediate</p>
		<p>Beta-ketoester cleavage; reverse of ester condensation</p>
		<p>Mixed ester condensation; R'' must have no alpha H's</p>
		<p>Mixed condensation- ketone with ester; beta-diketone product</p>
		<p>Dieckmann cyclization. Intramolecular ester condensation; 5 or 6 memb. rings only</p>
		<p>Intramolecular ketone with ester condensation; 5 or 6 memb. rings only</p>
		<p>Malonate ester alkylation R' can be 1° or 2°</p>

		<p>Decarboxylation of beta-carbonyl acid.</p> <p>"Malonic ester synthesis"</p> <p>Syn of substituted acids</p>
		<p>Acetoacetic ester alkylation</p> <p>R' can be 1° or 2°</p>
		<p>Decarboxylation of beta-carbonyl acid.</p> <p>"Acetoacetic ester synthesis"</p> <p>Syn of substituted ketones</p>
		<p>Michael reaction</p>
		<p>Pre-formed ester enolate</p> <p>R' must be 1° only</p>
		<p>Pre-formed ester enolate</p> <p>Mixed condensation with alde. or ketone</p>

Reactions of Amines (Carey, Chap. 22)		
Reaction	Product	Notes
$\begin{array}{c} \text{R}-\text{N}-\text{R}'' \\ \\ \text{R}' \end{array} \xrightleftharpoons[\text{NaOH}]{\text{H-A}}$	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}^{\oplus}-\text{R}'' \\ \\ \text{R}' \end{array} \quad \text{A}^{\ominus}$	<p>Ammonium salts; water soluble</p>
$\begin{array}{c} \text{R}-\text{N}-\text{H} \\ \\ \text{R}' \end{array} \xrightarrow[2. \text{NaOH}]{1. \text{R}'''-\text{X}}$ [NH ₃ , 1°, or 2°-amine]	$\begin{array}{c} \text{R}-\text{N}-\text{R}'' \\ \\ \text{R}' \end{array}$	<p>S_N2 substitution; 1° or 2° R''-X; excess starting amine required to avoid over-alkylation</p>
$\begin{array}{c} \text{R}-\text{N}-\text{R}'' \\ \\ \text{R}' \end{array} \xrightarrow{\text{R}'''-\text{X}}$ [3°-amine]	$\begin{array}{c} \text{R}''' \\ \\ \text{R}-\text{N}^{\oplus}-\text{R}'' \\ \\ \text{R}' \end{array} \quad \text{X}^{\ominus}$	<p>quaternary ammonium salts</p>
$\begin{array}{c} \text{R}-\text{N}-\text{H} \\ \\ \text{R}' \end{array} \xrightarrow[\text{H}_2, \text{Ni} \text{ [or NaBH}_3\text{CN]}]{\text{R}''-\text{C}(=\text{O})-\text{R}''', \text{H}^+}$ [NH ₃ , 1°, or 2°-amine]	$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{N}-\text{C}-\text{R}''' \\ \quad \\ \text{R}' \quad \text{R}'' \end{array}$	<p>Reductive amination of aldehyde or ketone; imine intermediate</p>
$\begin{array}{c} \text{R}-\text{N}-\text{H} \\ \\ \text{R}' \end{array} \xrightarrow[\text{pyridine}]{\text{R}''-\text{C}(=\text{O})\text{Cl} \text{ [or anhydride]}}$ [NH ₃ , 1°, or 2°-amine]	$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{N}-\text{C}-\text{R}'' \\ \quad \\ \text{R}' \quad \text{O} \end{array}$	<p>Prep. of 1°, 2° or 3° amides.</p>

		No reaction with 3°-amine
 <p><chem>Nc1ccccc1</chem> $\xrightarrow[\text{[NaNO}_2, \text{HX}]]{\text{HNO}_2}$ <chem>[N+]#Nc1ccccc1.[X-]</chem></p>		benzenediazonium salt; reactive intermediate
 <p><chem>Nc1ccccc1</chem> $\xrightarrow[2. \text{H}_2\text{O}, \Delta]{1. \text{HNO}_2}$ <chem>Oc1ccccc1</chem></p>		
 <p><chem>Nc1ccccc1</chem> $\xrightarrow[2. \text{CuX}]{1. \text{HNO}_2}$ <chem>Xc1ccccc1</chem> [X=F, Cl, Br, I]</p>		
 <p><chem>Nc1ccccc1</chem> $\xrightarrow[2. \text{CuCN}]{1. \text{HNO}_2}$ <chem>N#Cc1ccccc1</chem></p>		
 <p><chem>Nc1ccccc1</chem> $\xrightarrow[2. \text{H}_3\text{PO}_2]{1. \text{HNO}_2}$ <chem>c1ccccc1</chem></p>		