CHEM 238 Organic Chemistry

Ch10 Alcohol, Thiol Reactions

Reaction	Reactant	Condition	Product	Overall
Dehydration of alcohol	alcohol	phosphoric acid H3PO4	alkene, water	$\mathrm{ROH} \xrightarrow{\mathrm{H_3PO_4}} \text{alkene} + \mathrm{H_2O}$
Alcohol and HX	alcohol, hydrogen halide		alkyl halide, water	$\mathrm{ROH} + \mathrm{HX} \longrightarrow \mathrm{RX} + \mathrm{H_2O}$
Alcohol and sulfonate ester TsCl	alcohol, sulfonate ester TsCl, ROTs	pyridine, NaBr	alkyl bromide	$\mathrm{ROH} + \mathrm{TsCl} \xrightarrow{\text{pyridine}} \mathrm{R{-}OTs} \xrightarrow{\mathrm{NaBr}} \mathrm{RBr}$
Alkoxide and inorganic acid	alkoxide, inorganic acid (dimethyl sulfate)		ester, conjugate base	$\mathrm{RO^-} + \mathrm{(CH_3)_2SO_4} \longrightarrow \mathrm{ROCH_3} + \mathrm{CH_3SO_4^-}$
Alcohol and SOCl2	alcohol, thionyl chloride SOCl2	pyridine	alkyl chloride, sulfate dioxide, hydrogen chloride	$\mathrm{ROH} + \mathrm{SOCl_2} \xrightarrow[\text{pyridine}]{} \mathrm{RCl} + \mathrm{SO_2} + \mathrm{HCl}$
Alcohol and Ph3PBr2	alcohol, triphenylphosphine dibromine Ph3PBr2	DMF	alkyl bromide, base	$\mathrm{ROH} + \mathrm{Ph_3PBr_2} \xrightarrow[\text{DMF}]{} \mathrm{RBr} + \mathrm{Ph_3P^+O^-} + \mathrm{HBr}$
Oxidation of secondary 2nd alcohol	secondary alcohol, Cr(VI) (PCC)		ketone, Cr(III)	$\mathrm{ROH} + \mathrm{Cr(VI)\ (CrO_3, pyridine)} \longrightarrow \mathrm{R{=}O} + \mathrm{Cr(III)}$
Oxidation of primary 1st alcohol	primary alcohol	Cr2O4-	aldehyde, carboxylic acid	$\mathrm{RCH_2OH} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{Cr_2O_4^-}} \mathrm{RCH{=}O} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{Cr_2O_4^-}} \mathrm{RC{-}OH{=}O}$
Controlled oxidation of primary 1st alcohol	primary alcohol	PCC	aldehyde	$\mathrm{RCH_2OH} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{PCC}} \mathrm{RCH{=}O}$
Oxidation of primary alcohol	primary alcohol, potassium permaganate KMnO4		carboxylic acid's conjugate base	$\mathrm{RCH_2OH} + \mathrm{KMnO_4} + \mathrm{OH^-} \longrightarrow \mathrm{MnO_2} + \mathrm{RCOO^-} \xrightarrow{\mathrm{H_3O^+}} \mathrm{RCOOH}$
Oxidation of thiols/disulfide	thiols/disulfide, KMnO4/HNO3		sulfonic acid	$\mathrm{RSH} \xrightarrow{\mathrm{HNO_3}} \mathrm{RSO_3H}$
Oxidation of thiols	thiol, oxygen O2/iodine I2/bromine Br2		disulfide	$\mathrm{2\,RSH} + \mathrm{I_2} + \mathrm{2\,NaOH} \longrightarrow \mathrm{RSSR} + \mathrm{2\,NaI} + \mathrm{2\,H_2O}$

| Synthesis of alcohol

Reaction	Reactant	Condition	Product	Overall
Hydroboration-oxidation	alkene	HBR2, H2O2/OH-	alcohol	$\text{alkene} \xrightarrow[(2)\ \mathrm{H2O2/OH^-}]{(1)\ \mathrm{HBR2}} \mathrm{ROH}$
Oxymercuration-reduction	alkene	Hg(OAc)2/H2O, NaBH2/NaOH	alcohol	$\text{alkene} \xrightarrow[(2)\ \mathrm{NaBH2/NaOH}]{(1)\ \mathrm{Hg(OAc)2/H2O}} \mathrm{ROH}$

Reaction	Reactant	Condition	Product	Overall
Acid-cayalyzed hydration of alkene	alkene, water H2O	acid	alcohol	$\text{alkene} + H_2O \xrightarrow{H_3O^+} ROH$

Ch11 Ether, Sulfide, Epoxide, Glycol

| Synthesis, Cleavage of ether

Reaction	Reactant	Condition	Product	Overall
Williamson ether synthesis	alcohol	NaH, THF	ether	$ROH \xrightarrow[THF]{NaH} RO^- + Na^+ + H_2 \xrightarrow{XR'} ROR' + NaX + H_2$
Williamson sulfide synthesis	thiol	ROTs	sulfide	$RSH \xrightarrow[CH_3OH]{OH^-} RS^- + H_2O \xrightarrow{R'OTs} RSR' + H_2O + OTs^-$
Alkoxymercuration-reduction	alkene	Hg(OAc)2/HOR, NaBH4	ether	$\text{alkene} \xrightarrow[(2)\ NaBH_4]{(1)\ Hg(OAc)_2/HOR'} ROR'$
Primary 1st alcohol dehydration	primary alcohol	sulfuric acid H2SO4, heat	ether, water H2O	$2\,ROH \xrightarrow{H_2SO_4,\ \Delta} ROR + H_2O$
Tertiary 3rd alcohol dehydration	tertiary alcohol, primary alcohol	sulfuric acid H2SO4	ester, water H2O	$ROH + R'OH \xrightarrow{\text{dilute } H_2SO_4} ROR' + H_2O$
Alkene addition by tertiary alcohol	alkene, tertiary alcohol	sulfuric acid H2SO4	ether	$\text{alkene} + ROH \xrightarrow{\text{dilute } H_2SO_4} (CH_3)_3COR;$
Ether cleavage	ether, hydrogen halide	heat	alcohol, alkyl halide	$ROR' + HX \xrightarrow{\Delta} ROH + R'X$

| Synthesis of epoxide

Reaction	Reactant	Condition	Product	Overall
Oxidation of alkene with RCOOOH	alkene, peroxycarboxylic acid RCOOOH (MCPBA)		epoxide, carboxylic acid	$\text{alkene} + RCOOOH\ (MCPBA) \longrightarrow \text{epoxide} + RCOOH$
Cyclization of halohydrin	halohydrin (alcohol + alkyl halide RX), base		epoxide, water H2O	$\text{halohydrin}\ (OH{-}C{-}C{-}X) + NaOH \longrightarrow \text{epoxide} + NaX + H_2O$

| Ring opening of epoxide

Reaction	Reactant	Condition	Product	Overall
Base ring opening	epoxide, alcohol	alkoxide	alcohol-ether	$\text{epoxide} + R'OH \xrightarrow{R'O^-} \text{ester}{-}\text{alcohol}$
Acid ring opening	epoxide, alcohol	acid	alcohol-ether	$\text{epoxide},\ R'OH \xrightarrow{H_3O^+} \text{alcohol}{-}\text{ether}$
Grignard organometallic ring opening	Grignard reagent MgBr, epoxide	ether, heat, acid H3O+	alcohol	$\text{epoxide} + R'MgBr \xrightarrow[H_3O^+]{(1)\ \text{ether},\ \text{heat}} R'CR_2CR_2OH$

| Preparation, Cleavage of glycol

Reaction	Reactant	Condition	Product	Overall
Acid ring opening (hydrolysis) of epoxide	epoxide, water H2O	acid	glycol	$\text{epoxide} + \text{H}_2\text{O} \xrightarrow{\text{acid}} \text{glycol}$
Oxidation of alkene by OsO4	alkene, osmium tetroxide OsO4	water H2O, NaHSO3	glycol	$\text{R}_2\text{C}{=}\text{CR}_2 + \text{OsO}_4 \xrightarrow[\text{NaHSO3}]{\text{H2O}} \text{glycol} + \text{OsO}_3(\text{OH})_2$
Alkene + KMnO4	alkene, potassium permanganate KMnO4	water, acetone	glycol, MnO2	$\text{alkene} + \text{KMnO}_4 \xrightarrow[\text{acetone}]{\text{H2O, OH}^-} \text{glycol} + \text{MnO}_2$
Glycol cleavage	glycol, periodic acid H5IO6	HOAc	aldehyde, ketone, water	$\text{glycol} + \text{H}_5\text{IO}_6 \xrightarrow{\text{HOAc}} \text{R}'{-}\text{CH}{=}\text{O} + \text{R}{-}\text{CR}{=}\text{O} + 2\,\text{H}_2\text{O} + \text{HIO}_3\text{H}_2\text{O}$

| Oxonium salt

Reaction	Reactant	Condition	Product	Overall
Oxonium salt	nucleophile, oxonium salt		alcohol	$\text{Nu}^- + \text{R}_3\text{O}^+ \longrightarrow \text{ROH} + \text{H}_2\text{O}$

Ch14 Alkyne Reactions

Reaction	Reactant	Condition	Product	Overall
Alkyne addition	alkyne, hydrogen halide		alkene halide	$\text{C}{\equiv}\text{C} + \text{HX} \longrightarrow \text{XC}{=}\text{C}$
Hydration of alkyne	alkyne, water	mercury ion, sulfuric acid H2SO4	ketone	$\text{RC}{\equiv}\text{CH} + \text{H}_2\text{O} \xrightarrow{\text{Hg}^{2+},\ \text{H}_2\text{SO}_4} \text{RC}{=}\text{OCH}_3$
Hydroboration-oxidation of symmetric alkyne	symmetric alkyne	borane BH3, THF, hydrogen peroxide	ketone	$\text{R}{-}\text{C}{\equiv}\text{C}{-}\text{R} \xrightarrow[(2)\ \text{H2O2/OH}^-]{(1)\ \text{BH3/THF}} \text{R}{-}\text{CH}_2{-}\text{C}{=}\text{O}{-}\text{R}$
Hydroboration-oxidation of asymmetric alkyne	asymmetric 1-alkyne	disiamylborane, THF, hydrogen peroxide	aldehyde	$\text{R}{-}\text{C}{\equiv}\text{C}{-}\text{H} \xrightarrow[(2)\ \text{H2O2/OH}^-]{(1)\ (\text{branch})_2\text{BH/THF}} \text{R}{-}\text{CH}_2{-}\text{C}{=}\text{O}{-}\text{H}$
Catalytic hydrogenation of alkyne	alkyne	hydrogen gas H2, catalyst	cis alkene	$\text{RC}{=}\text{CR} \xrightarrow{\text{H2, catalyst}} \text{RCH}{=}\text{HCR}$
Catalytic hydrogenation of alkene	alkene	hydrogen gas H2, catalyst	alkane	$\text{RCH}{=}\text{HCR} \xrightarrow{\text{H2, catalyst}} \text{RCH}_2{=}\text{H}_2\text{CR}$
Controlled catalytic hydrogenation of alkyne	alkyne	Lindlar catalyst/(Pd/C), pyridine	cis alkene	$\text{RC}{=}\text{CR} \xrightarrow[\text{or Pd/C, pyridine}]{\text{Lindlar catalyst Pd/CaCO3+Pb(OAc)2}} \text{RCH}{=}\text{HCR}$
Reduction of alkyne with Na and NH3	alkyne, sodium, liquid ammonia		trans alkene, sodium ion, azanide	$\text{RC}{=}\text{CR} + 2\,\text{Na} + 2\,\text{NH}_3 \longrightarrow \text{RCH}{=}\text{HCR} + 2\,\text{Na}^+ + 2\,\text{NH}_2^-$

Reaction	Reactant	Condition	Product	Overall
Grignard reaction of alkyne	1-alkyne, Grignard reagent	THF	acetylenic Grignard reagent, hydrocarbon	$\mathrm{RC{\equiv}CR + R'MgBr \xrightarrow{THF} RC{\equiv}CMgBr + R'}$
Alkyne in SN2 rxn	alkane halide, acetylenic anion		alkyne, halide ion	$\mathrm{RX + C{\equiv}CR^- \longrightarrow RC{\equiv}CR + X^-}$

Ch15 Diene Reactions

Reaction	Reactant	Condition	Product	Overall
Diels-Alder Rxn	diene, alkene (dienophile)		ring	$\mathrm{diene + dienophile \longrightarrow ring}$
Addition of HX to conjugated diene	conjugated diene, hydrogen halide		alkene halide	$\mathrm{conj \cdot diene + HX \longrightarrow mixed\ alkene\ halide}$

Ch16 Benzene Reactions

Reaction	Reactant	Condition	Product	Overall
Halogenation of benzene	benzene, halide gas X2	iron/iron(iii) bromide FeBr3	benzene halide, hydrogen halide	$\mathrm{Ph + X_2 \xrightarrow{FeBr3/Fe} PhX + HX}$
Nitration of benzene	benzene, nitric acid HNO3	sulfuric acid H2SO4	nitrobenzene, water	$\mathrm{Ph + HNO_3 \xrightarrow{H2SO4} PhNO_2 + H_2O}$
Sulfonation of benzene	benzene, sulfur trioxide	fuming sulfuric acid H2SO4	benzenesulfuric acid	$\mathrm{Ph + SO_3 \xrightarrow{fuming\ H2SO4} PhSO_3H}$
Friedel-Crafts alkylation of benzene	benzene, alkyl chloride	aluminum chloride AlCl3	alkyl benzene, hydrogen chloride	$\mathrm{Ph + RCl \xrightarrow{AlCl3} PhR + HCl}$
Friedel-Crafts acylation of benzene	benzene, acyl chloride	aluminum chloride AlCl3, water	ketone, hydrogen chloride	$\mathrm{Ph + Cl{-}CR{=}O \xrightarrow[(2)H_2)]{(1)\ AlCl3} Ph{-}C{=}OCH_3 + HCl}$
Hydrogenation of benzene	benzene, hydrogen gas H2	Ni	cyclohexane	$\mathrm{Ph + 3\,H_2 \xrightarrow[175^oC,\ 180\ atm]{Ni} cyclohexane}$
Hydrogenation of benzene derivatives	benzene derivative, hydrogen gas H2	Ni	substituted cyclohexane	$\mathrm{PhR + 3\,H_2 \xrightarrow[175^oC,\ 180\ atm]{Ni} cyclohexane{-}R}$

Ch17 Allylic/Benzylic Reactions

Reaction	Reactant	Condition	Product	Overall
Radical bromonation of allylic/benzylic hydrogen	allylic/benzylic species, bromine gas Br2	light hv	allylic/benzylic bromide, hydrogen bromide	$\mathrm{PhCH_3 + Br_2 \xrightarrow{light\ hv} PhCH_2Br + HBr}$ $\mathrm{CH_3{-}CH_2{=}CH_2 \xrightarrow{light\ hv} BrCH_2{-}CH_2{=}CH_2}$

Reaction	Reactant	Condition	Product	Overall
Controlled radical bromonation of allylic/benzylic hydrogen	allylic/benzylic species, NBS (N-bromosuccinimide)	heat/light, peroxide	allylic/benzylic bromide, succinimide	$\mathrm{PhCH_3 + NBS \xrightarrow[CCl_4]{\text{heat/light, peroxide}} PhCH_2Br}$ $\mathrm{CH_3{-}CH_2{=}CH_2 + NBS \xrightarrow{\text{light hv}} BrCH_2{-}CH_2{=}CH_2 + \text{succinimide}}$
Allylic/benzylic Grignard Reagent	alkene bromide Br, magnesium Mg		alkene, MgBrOH	$\longrightarrow$ see Ch 17 allylic Grignard reagent
Allylic/benzylic E2 elimination	allylic/benzylic bromide	EtOH, Na+, EtO-	alkene	$\mathrm{Ph{-}CH_2CH_2{-}Br \xrightarrow[EtOH]{Na^+,\ EtO^-} Ph{-}CH_2CH_2{-}OEt}$
Oxidation of allylic/benzylic alcohol with MnO2	allylic/benzylic alcohol, manganese dioxide MnO2	CH2Cl2	aldehyde/ketone, Mn(OH)2	$\mathrm{PhCH_2OH + MnO_2 \xrightarrow[CH_2Cl_2]{} PhCH{=}O + Mn(OH)_2}$ $\mathrm{H_2C{=}CH{-}CH_2OH + MnO_2 \xrightarrow[CH_2Cl_2]{} H_2C{=}CH{-}CH_2{=}O + Mn(OH)_2}$
Benzylic oxidation of alkylbenzene	alkylbenzene	Cr(VI): Na2CrO7/CrO3; Mn(VII): KMnO4; O2 + catalyst	benzylic carboxylic acid	$\mathrm{PhR \xrightarrow[\text{or } KMnO_4 \text{ or } O_2 + \text{catalyst}]{Na_2CrO_7/CrO_3} PhCOOH}$
Biosynthesis of terpene	isopentenyl pyrophosphate IPP, gamma,gamma-dimethylallyl pyrophosphate DMAP	prenyl transferase	terpene, HOPP	$\mathrm{IPP + DMAP \xrightarrow{\text{prenyl transferase } SN_1} \text{terpene, HOPP}}$

Ch18 Vinylic/Aryl Halide Reactions

Reaction	Reactant	Condition	Product	Overall
Vinylic/aryl halide under SN1, SN2 conditions	Vinylic/aryl halide	SN1, SN2	no reaction	$\mathrm{CH_2{=}CHX + Nu \xrightarrow{SN_1,\ SN_2} \text{no reaction}}$ $\mathrm{PhX + Nu \xrightarrow{SN_1,\ SN_2} \text{no reaction}}$
Elimination of vinylic halide	vinylic halide, nucleophile (hydroxide)	harsh conditions, high temp	vinylic alkyne, bromide, water	$\mathrm{Ph{-}CH{=}CH{-}Br + KOH \xrightarrow[200^\circ C]{} Ph{-}C{\equiv}C{-}H + KBr + H_2O}$
Nucleophilic aromatic substitution of aryl halide	nitro aryl halide, nucleophile		nitro aryl nucleophile: halide ion	$\mathrm{O_2N{-}Ph{-}X + Nu^- \longrightarrow O_2N{-}Ph{-}Nu + X^-}$
Heck reaction (aryl)	aryl bromide/iodide, alkene	Pd(0) catalyst (Pd(OAc)2, Pd(PPh3)4)	aryl alkene, hydrogen bromide	$\mathrm{PhBr + alkene \xrightarrow{Pd(0)} Ph{-}alkene + HBr}$
Heck reaction (general)	alkyl halide + alkene	Pd(0) catalyst (Pd(OAc)2, Pd(PPh3)4)	alkene, hydrogen bromide	$\mathrm{R_1X + alkene{-}R_2 \xrightarrow{PdL_4} R_1{-}alkene{-}R_2 + HX}$
Suzuki coupling	aryl boronic acid, aryl halide, sodium hydroxide	Pd(OAc)2, PPh3, Na2CO3	biaryl compound, NaBr, B(OH)2	$\mathrm{RB(OH)_2 + R'X + NaOH \xrightarrow{Pd(OAc)_2,\ PPh_3,\ Na_2CO_3} RR' + NaBr + B(OH)_2}$

Reaction	Reactant	Condition	Product	Overall
Oxidation of phenol	phenol -> semiquinone	Na2Cr2O7, H2SO4	quinone	$\mathrm{Ph(OH)_2} \xrightarrow{\mathrm{Na_2Cr_2O_7,\ H_2SO_4}} \mathrm{quinone}$
Bromination of phenol	phenol, bromine gas	CCl4, Hbr, water H2O	phenol bromide	$\mathrm{PhOH} + n\,\mathrm{Br_2} \xrightarrow{\text{various conditions}} \mathrm{PhOH{-}Br}_n + n\,\mathrm{HBr}$
Nitration of phenol	phenol	nitric acid HNO3	nitric phenol	$\mathrm{PhOH} \xrightarrow{\mathrm{HNO_3}} \mathrm{PhOH{-}NO_2} + \mathrm{H_2O}$
Friedel-Crafts alkylation	phenol, alcohol	sulfuric acid H2SO4	alkyl phenol, water H2O	$\mathrm{PhOH} + \mathrm{ROH} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{RPhOH} + \mathrm{H_2O}$
Friedel-Crafts acylation	phenol, AlCl3, acyl chloride	PhNO2	acyl phenol	$\mathrm{PhOH} + \mathrm{AlCl_3} + \mathrm{RC{=}O{-}Cl} \xrightarrow{\mathrm{PhNO_2}} \mathrm{PhOH{-}CR{=}O}$