CHEM 238 Organic Chemistry Reactions

Organized by Teng-Jui Lin

Warning

- **WARNING: These equations are hand-typed and for personal reference use, so it is guaranteed to have some mistakes, both innocent and unforgivable. Therefore, use with caution!**
- By using this equation sheet, you accept the risk associated with potential mistakes.
- If you find any mistakes, I welcome you to raise an issue.
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Ch10 Alcohol, Thiol Reactions

Reaction	Reactant	Condition	Product	Overall
Dehydration of alcohol	alcohol	phosphoric acid H3PO4	alkene, water	$\mathrm{ROH} \xrightarrow{\mathrm{H_3PO_4}} \mathrm{alkene} + \mathrm{H_2O}$
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	$\mathrm{ROH} + \mathrm{TsCl} \xrightarrow{\mathrm{pyridine}} \mathrm{R{-}OTs} \xrightarrow{\mathrm{NaBr}} \mathrm{RBr}$
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	$\mathrm{ROH} + \mathrm{SOCl_2} \xrightarrow[\mathrm{pyridine}]{} \mathrm{RCl} + \mathrm{SO_2} + \mathrm{HCl}$
Alcohol and Ph3PBr2	alcohol, triphenylphosphine dibromine Ph3PBr2	DMF	alkyl bromide, base	$\mathrm{ROH} + \mathrm{Ph_3PBr_2} \xrightarrow[\mathrm{DMF}]{} \mathrm{RBr} + \mathrm{Ph_3P^+O^-} + \mathrm{HBr}$
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	$\mathrm{RCH_2OH} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{Cr_2O_4^-}} \mathrm{RCH{=}O} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{Cr_2O_4^-}} \mathrm{RC{-}OH{=}O}$

Reaction	Reactant	Condition	Product	Overall
Controlled oxidation of primary 1st alcohol	primary alcohol	PCC	aldehyde	$\mathrm{RCH_2OH \xrightarrow[CH_2Cl_2]{PCC} RCH{=}O}$
Oxidation of primary alcohol	primary alcohol, potassium permaganate KMnO4		carboxylic acid's conjugate base	$\mathrm{RCH_2OH + KMnO_4 + OH^- \longrightarrow MnO_2 + RCOO^- \xrightarrow{H_3O^+} RCOOH}$
Oxidation of thiols/disulfide	thiols/disulfide, KMnO4/HNO3		sulfonic acid	$\mathrm{RSH \xrightarrow{HNO_3} RSO_3H}$
Oxidation of thiols	thiol, oxygen O2/iodine I2/bromine Br2		disulfide	$\mathrm{2\,RSH + I_2 + 2\,NaOH \longrightarrow RSSR + 2\,NaI + 2\,H_2O}$

Synthesis of alcohol

Reaction	Reactant	Condition	Product	Overall
Hydroboration-oxidation	alkene	HBR2, H2O2/OH-	alcohol	$\mathrm{alkene \xrightarrow[(2)\ H_2O_2/OH^-]{(1)\ HBR_2} ROH}$
Oxymercuration-reduction	alkene	Hg(OAc)2/H2O, NaBH2/NaOH	alcohol	$\mathrm{alkene \xrightarrow[(2)\ NaBH_2/NaOH]{(1)\ Hg(OAc)_2/H_2O} ROH}$
Acid-cayalyzed hydration of alkene	alkene, water H2O	acid	alcohol	$\mathrm{alkene + H_2O \xrightarrow{H_3O^+} ROH}$

Ch11 Ether, Sulfide, Epoxide, Glycol

Synthesis, Cleavage of ether

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

Synthesis of epoxide

Reaction	Reactant	Condition	Product	Overall
Oxidation of alkene with RCOOOH	alkene, peroxycarboxylic acid RCOOOH (MCPBA)		epoxide, carboxylic acid	$\mathrm{alkene + RCOOOH\ (MCPBA) \longrightarrow epoxide + RCOOH}$

Reaction	Reactant	Condition	Product	Overall
Cyclization of halohydrin	halohydrin (alcohol + alkyl halide RX), base		epoxide, water H2O	$\mathrm{halohydrin\ (OH{-}C{-}C{-}X) + NaOH \longrightarrow epoxide + NaX + H_2O}$

Ring opening of epoxide

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

Preparation, Cleavage of glycol

Reaction	Reactant	Condition	Product	Overall
Acid ring opening (hydrolysis) of epoxide	epoxide, water H2O	acid	glycol	$\mathrm{epoxide + H_2O \xrightarrow{acid} glycol}$
Oxidation of alkene by OsO4	alkene, osmium tetroxide OsO4	water H2O, NaHSO3	glycol	$\mathrm{R_2C{=}CR_2 + OsO_4 \xrightarrow[NaHSO_3]{H_2O} glycol + OsO_3(OH)_2}$
Alkene + KMnO4	alkene, potassium permanganate KMnO4	water, acetone	glycol, MnO2	$\mathrm{alkene + KMnO_4 \xrightarrow[acetone]{H_2O,\ OH^-} glycol + MnO_2}$
Glycol cleavage	glycol, periodic acid H5IO6	HOAc	aldehyde, ketone, water	$\mathrm{glycol + H_5IO_6 \xrightarrow{HOAc} R'{-}CH{=}O + R{-}CR{=}O + 2\,H_2O + HIO_3H_2O}$

Oxonium salt

Reaction	Reactant	Condition	Product	Overall
Oxonium salt	nucleophile, oxonium salt		alcohol	$\mathrm{Nu^- + R_3O^+ \longrightarrow ROH + H_2O}$

Ch14 Alkyne Reactions

Reaction	Reactant	Condition	Product	Overall
Alkyne addition	alkyne, hydrogen halide		alkene halide	$\mathrm{C{\equiv}C + HX \longrightarrow XC{=}C}$
Hydration of alkyne	alkyne, water	mercury ion, sulfuric acid H2SO4	ketone	$\mathrm{RC{\equiv}CH + H_2O \xrightarrow{Hg^{2+},\ H_2SO_4} RC{=}OCH_3}$
Hydroboration-oxidation of symmetric alkyne	symmetric alkyne	borane BH3, THF, hydrogen peroxide	ketone	$\mathrm{R{-}C{\equiv}C{-}R \xrightarrow[(2)\ H_2O_2/OH^-]{(1)\ BH_3/THF} R{-}CH_2{-}C{=}O{-}R}$
Hydroboration-oxidation of asymmetric	asymmetric 1-alkyne	disiamylborane, THF, hydrogen peroxide	aldehyde	$\mathrm{R{-}C{\equiv}C{-}H \xrightarrow[(2)\ H_2O_2/OH^-]{(1)\ (branch)_2BH/THF} R{-}CH_2{-}C{=}O{-}H}$

Reaction	Reactant	Condition	Product	Overall
alkyne				
Catalytic hydrogenation of alkyne	alkyne	hydrogen gas H2, catalyst	cis alkene	$\mathrm{RC{\equiv}CR \xrightarrow{H_2,\ catalyst} RCH{=}HCR}$
Catalytic hydrogenation of alkene	alkene	hydrogen gas H2, catalyst	alkane	$\mathrm{RCH{=}HCR \xrightarrow{H_2,\ catalyst} RCH_2{-}H_2CR}$
Controlled catalytic hydrogenation of alkyne	alkyne	Lindlar catalyst/(Pd/C), pyridine	cis alkene	$\mathrm{RC{\equiv}CR \xrightarrow[or\ Pd/C,\ pyridine]{Lindlar\ catalyst\ Pd/CaCO_3{+}Pb(OAc)_2} RCH{=}HCR}$
Reduction of alkyne with Na and NH3	alkyne, sodium, liquid ammonia		trans alkene, sodium ion, azanide	$\mathrm{RC{\equiv}CR + 2\,Na + 2\,NH_3 \longrightarrow RCH{=}HCR + 2\,Na^+ + 2\,NH_2{}^-}$
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	$\mathrm{Ph + X_2 \xrightarrow{FeBr_3/Fe} PhX + HX}$
Nitration of benzene	benzene, nitric acid HNO3	sulfuric acid H2SO4	nitrobenzene, water	$\mathrm{Ph + HNO_3 \xrightarrow{H_2SO_4} PhNO_2 + H_2O}$
Sulfonation of benzene	benzene, sulfur trioxide	fuming sulfuric acid H2SO4	benzenesulfuric acid	$\mathrm{Ph + SO_3 \xrightarrow{fuming\ H_2SO_4} PhSO_3H}$
Friedel-Crafts alkylation of benzene	benzene, alkyl chloride	aluminum chloride AlCl3	alkyl benzene, hydrogen chloride	$\mathrm{Ph + RCl \xrightarrow{AlCl_3} PhR + HCl}$
Friedel-Crafts acylation of benzene	benzene, acyl chloride	aluminum chloride AlCl3, water	ketone, hydrogen chloride	$\mathrm{Ph + Cl{-}CR{=}O \xrightarrow[(2)H_2)]{(1)\ AlCl_3} Ph{-}C{=}OCH_3 + HCl}$
Hydrogenation of benzene	benzene, hydrogen	Ni	cyclohexane	$\mathrm{Ph + 3\,H_2 \xrightarrow[175^oC,\ 180\,atm]{Ni} cyclohexane}$

Reaction	Reactant	Condition	Product	Overall
	gas H2			
Hydrogenation of benzene derivatives	benzene derivative, hydrogen gas H2	Ni	substituted cyclohexane	$\mathrm{PhR} + 3\,\mathrm{H_2} \xrightarrow[175^{o}\mathrm{C},\ 180\,\mathrm{atm}]{\mathrm{Ni}} \mathrm{cyclohexane{-}R}$

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	$\mathrm{PhCH_3} + \mathrm{Br_2} \xrightarrow{\text{light hv}} \mathrm{PhCH_2Br} + \mathrm{HBr}$ $\mathrm{CH_3{-}CH_2{=}CH_2} \xrightarrow{\text{light hv}} \mathrm{BrCH_2{-}CH_2{=}CH_2}$
Controlled radical bromonation of allylic/benzylic hydrogen	allylic/benzylic species, NBS (N-bromosuccinimide)	heat/light, peroxide	allylic/benzylic bromide, succinimide	$\mathrm{PhCH_3} + \mathrm{NBS} \xrightarrow[\mathrm{CCl_4}]{\text{heat/light, peroxide}} \mathrm{PhCH_2Br}$ $\mathrm{CH_3{-}CH_2{=}CH_2} + \mathrm{NBS} \xrightarrow{\text{light hv}} \mathrm{BrCH_2{-}CH_2{=}CH_2} + \mathrm{succin}$
Allylic/benzylic Grignard Reagent	alkene bromide Br, magnesium Mg		alkene, MgBrOH	$\longrightarrow \text{see Ch 17 allylic Grignard reagent}$
Allylic/benzylic E2 elimination	allylic/benzylic bromide	EtOH, Na+, EtO-	alkene	$\mathrm{Ph{-}CH_2CH_2{-}Br} \xrightarrow[\mathrm{EtOH}]{\mathrm{Na^+,\ EtO^-}} \mathrm{Ph{-}CH_2CH_2{-}OEt}$
Oxidation of allylic/benzylic alcohol with MnO2	allylic/benzylic alcohol, manganese dioxide MnO2	CH2Cl2	aldehyde/ketone, Mn(OH)2	$\mathrm{PhCH_2OH} + \mathrm{MnO_2} \xrightarrow[\mathrm{CH_2Cl_2}]{} \mathrm{PhCH{=}O} + \mathrm{Mn(OH)_2}$ $\mathrm{H_2C{=}CH{-}CH_2OH} + \mathrm{MnO_2} \xrightarrow[\mathrm{CH_2Cl_2}]{} \mathrm{H_2C{=}CH{-}CH_2{=}O} + \mathrm{M}$
Benzylic oxidation of alkylbenzene	alkylbenzene	Cr(VI): Na2CrO7/CrO3; Mn(VII): KMnO4; O2 + catalyst	benzylic carboxylic acid	$\mathrm{PhR} \xrightarrow[\text{or } \mathrm{KMnO_4} \text{ or } \mathrm{O_2}+\text{catalyst}]{\mathrm{Na_2CrO_7/CrO_3}} \mathrm{PhCOOH}$
Biosynthesis of terpene	isopentenyl pyrophosphate IPP, gamma,gamma-dimethylallyl pyrophosphate DMAP	prenyl transferase	terpene, HOPP	$\mathrm{IPP} + \mathrm{DMAP} \xrightarrow{\text{prenyl transferase } \mathrm{SN_1}} \text{terpene, HOPP}$

Ch18 Vinylic/Aryl Halide Reactions

Reaction	Reactant	Condition	Product	Overall
Vinylic/aryl halide under SN1, SN2 conditions	Vinylic/aryl halide	SN1, SN2	no reaction	$\mathrm{CH_2{=}CHX} + \mathrm{Nu} \xrightarrow{\mathrm{SN_1,\ SN_2}} \text{no reaction}$ $\mathrm{PhX} + \mathrm{Nu} \xrightarrow{\mathrm{SN_1,\ SN_2}} \text{no reaction}$
Elimination of vinylic halide	vinylic halide, nucleophile (hydroxide)	harsh conditions, high temp	vinylic alkyne, bromide, water	$\mathrm{Ph{-}CH{=}CH{-}Br} + \mathrm{KOH} \xrightarrow[200^{\circ}\mathrm{C}]{} \mathrm{Ph{-}C{\equiv}C{-}H} + \mathrm{KBr} + \mathrm{H_2O}$
Nucleophilic aromatic substitution of aryl	nitro aryl halide, nucleophile		nitro aryl nucleophile: halide ion	$\mathrm{O_2N{-}Ph{-}X} + \mathrm{Nu^-} \longrightarrow \mathrm{O_2N{-}Ph{-}Nu} + \mathrm{X^-}$

Reaction	Reactant	Condition	Product	Overall
halide				
Heck reaction (aryl)	aryl bromide/iodide, alkene	Pd(0) catalyst (Pd(OAc)2, Pd(PPh3)4)	aryl alkene, hydrogen bromide	$\mathrm{PhBr} + \mathrm{alkene} \xrightarrow{\mathrm{Pd(0)}} \mathrm{Ph{-}alkene} + \mathrm{HBr}$
Heck reaction (general)	alkyl halide + alkene	Pd(0) catalyst (Pd(OAc)2, Pd(PPh3)4)	alkene, hydrogen bromide	$\mathrm{R_1X} + \mathrm{alkene{-}R_2} \xrightarrow{\mathrm{PdL_4}} \mathrm{R_1{-}alkene{-}R_2} + \mathrm{HX}$
Suzuki coupling	aryl boronic acid, aryl halide, sodium hydroxide	Pd(OAc)2, PPh3, Na2CO3	biaryl compound, NaBr, B(OH)2	$\mathrm{RB(OH)_2} + \mathrm{R'X} + \mathrm{NaOH} \xrightarrow{\mathrm{Pd(OAc)_2,\ PPh_3,\ Na_2CO_3}} \mathrm{RR'} + \mathrm{NaBr} + \mathrm{B(OH)_2}$
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	$\mathrm{PhOH} + \mathrm{AlCl_3} + \mathrm{RC{=}O{-}Cl} \xrightarrow{\mathrm{PhNO_2}} \mathrm{PhOH{-}CR{=}O}$