

Table 1

Reagent code list for preparation
and reactions of alkenes

	<u>REACTIONS OF</u>	<u>ALKENES</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING MATERIAL</u>	<u>CODE</u>	<u>REACTIVE SPECIES</u>	<u>PRODUCT</u>	<u>STEREOCHEMISTRY</u>
ALKENE	HCl HBr or HI/H ₂ O	HCL, HBr or HI	ALKYL HALIDE	MARKONIKOV
ALKENE	Hg(OAC) ₂ /NaBH ₄ or H ₂ O/H ⁺	HOH	ALCOHOL	MARKONIKOV
ALKENE	Br ₂ /CCl ₄ or Cl ₂ /CCl ₄	Br ₂ , Cl ₂	DIHALIDE	TRANS
ALKENE	Br ₂ /H ₂ O or Cl ₂ /H ₂ O	HOBr, HOCl	HALOHYDRIN	MARKONIKOV*, TRANS *Cl ⁺ , Br ⁺ = H ⁺
ALKENE	RCOOH (peracid)	O	EPOXIDE	RETENTION OF ALKENE STEREOCHEMISTRY
ALKENE	Hg(OAC) ₂ ,H ₂ O,THF NaBH ₄	HOH	ALCOHOL	MARKONIKOV
1,2-DIOL	HIO ₄	O	ALDEHYDES	
ALKENE	BH ₃ /THF OH ⁻ , H ₂ O ₂ , H ₂ O	HOH	ALCOHOL	ANTI-MARKONIKOV, CIS
ALKENE	H ₂ /Pt or Pd, or D ₂ /Pt or Pd	H ₂ , D ₂	ALKANE	CIS
ALKENE	OSO ₄	2 OH ADD	DIOL	CIS
ALKENE	O ₃ /Zn	O	ALDEHYDE OR KETONE SEE CHART	
ALKENE	KMNO ₄ /H ₃ O ⁺	O	ACID OR CO ₂ SEE CHART	
ALKENE	CHCl ₃ /OH ⁻	CCl ₂ , CARBENE	DICHLORO CYCLOPROPANE	RETENTION OF ALKENE STEREOCHEMISTRY
ALKENE	CH ₂ I ₂ /Zn	CH ₂ , CARBENE	CYCLOPROPANE	RETENTION OF ALKENE STEREOCHEMISTRY

Table 11

Reagent code list for preparation
and reactions of alkynes

STARTING MATERIAL	CODE	REACTIVE SPECIES	PRODUCT	STEREOCHEMISTRY
TERMINAL ALKYNE $R-C\equiv CH$	HCl HBr or HI/H ₂ O, 1 MOLE	HCl, HBr or HI	VINYL HALIDE $R-\underset{\substack{ \\ Cl}}{C}=CH_2$	MARKONIKOV
TERMINAL ALKYNE $R-C\equiv CH$	HCl HBr or HI/H ₂ O, 2 MOLES	HCl, HBr or HI	2,2-DIHALOALKANE $R-\underset{\substack{ \\ Cl}}{\underset{\substack{ \\ Cl}}{C}}-CH_3$	MARKONIKOV
TERMINAL ALKYNE $R-C\equiv CH$	Hg ⁺² /H ₂ SO ₄ or H ₂ O/H ⁺	HOH	METHYL KETONE RCOCH ₃ VIA ENOL $R-\underset{\substack{ \\ OH}}{C}=CH_2$	MARKONIKOV
TERMINAL ALKYNE $R-C\equiv CH$	Br ₂ /CCl ₄ or Cl ₂ /CCl ₄ 1 MOLE	Br ₂ , Cl ₂ 1 MOLE	TRANS-DIHALOALKENE $R-\underset{\substack{ \\ Br}}{C}=\underset{\substack{ \\ Cl}}{CH}$	TRANS
TERMINAL ALKYNE $R-C\equiv CH$	Br ₂ /CCl ₄ or Cl ₂ /CCl ₄ 2 MOLES	Br ₂ , Cl ₂ 2 MOLES	TETRAHALOALKANE $R-\underset{\substack{ \\ Br}}{\underset{\substack{ \\ Br}}{\underset{\substack{ \\ Cl}}{\underset{\substack{ \\ Cl}}{C}}}}-CH_3$	NOT APPLICABLE
TERMINAL ALKYNE $R-C\equiv CH$	BH ₃ OR ISOAMYLBORANE/THF OH ⁻ , H ₂ O ₂ , H ₂ O	HOH	ALDEHYDE RCH ₂ CHO VIA ENOL RCH=CHOH	ANTI-MARKONIKOV
TERMINAL ALKYNE $R-C\equiv CH$	H ₂ /Pt OR Pd (2MOLES)	H ₂ , 2 MOLES	ALKANE RCH ₂ CH ₃	NOT APPLICABLE
TERMINAL ALKYNE $R-C\equiv CH$	1) NaNH ₂ , 2) R'-X R= PRIMARY HALIDE X= Br or Cl	R'-X	INTERNAL ALKYNE $R-C\equiv CR'$	NOT APPLICABLE
INTERNAL ALKYNE $R-C\equiv CR'$	HCl HBr or HI/H ₂ O, 1 MOLE	HCl, HBr or HI 1MOLE	VINYL HALIDE $RC=\underset{\substack{ \\ Cl}}{CHR'}$	NOT APPLICABLE

STARTING MATERIAL	CODE	REACTIVE SPECIES	PRODUCT	STEREOCHEMISTRY
INTERNAL ALKYNE $R-C\equiv CR'$	HCl HBr or HI/H ₂ O, 2 MOLE	HCl, HBr or HI 2 MOLES	DIHALOALKANE $\begin{array}{c} \text{X} \quad \text{X} \\ \quad \\ R-C-C-R' \\ \quad \\ \text{X} \quad \text{X} \end{array}$	NOT APPLICABLE
INTERNAL ALKYNE $R-C\equiv CR'$	Hg ⁺² /H ₂ SO ₄ or H ₂ O/H+	HOH	KETONE $R-CO-CH_2-R'$ VIA ENOL $\begin{array}{c} R-C=CR' \\ \quad \\ H \quad H \end{array}$	NOT APPLICABLE
INTERNAL ALKYNE $R-C\equiv CR'$	Br ₂ /CCl ₄ or Cl ₂ /CCl ₄ 1 MOLE	Br ₂ , Cl ₂ , 1 MOLE	TRANS-DIHALOALKENE $\begin{array}{c} \text{X} \quad \text{X} \\ \diagdown \diagup \\ R-C=C-R' \\ \diagup \diagdown \\ \text{X} \quad \text{X} \end{array}$	TRANS
INTERNAL ALKYNE $R-C\equiv CR'$	Br ₂ /CCl ₄ or Cl ₂ /CCl ₄ 2 MOLES	Br ₂ , Cl ₂ 2 MOLES	TETRAHALOALKANE $\begin{array}{c} \text{X} \quad \text{X} \quad \text{X} \quad \text{X} \\ \quad \quad \quad \\ R-C-C-R' \\ \quad \quad \quad \\ \text{X} \quad \text{X} \quad \text{X} \quad \text{X} \end{array}$	NOT APPLICABLE
INTERNAL ALKYNE $R-C\equiv CR'$	BH ₃ OR ISOAMYLBORANE/THF OH ⁻ , H ₂ O ₂ , H ₂ O	HOH	KETONE $R-CO-CH_2-R'$ VIA ENOL $\begin{array}{c} R-C=CHR' \\ \quad \\ H \quad H \end{array}$	NOT APPLICABLE
INTERNAL ALKYNE $R-C\equiv CR'$	H ₂ /Pd/BaSO ₄ LINDLAR CATALYST	H ₂ , 1 MOLE	CIS-ALKENE $\begin{array}{c} H \quad H \\ \quad \\ R-C=C-R' \end{array}$	CIS
INTERNAL ALKYNE $R-C\equiv CR'$	Na OR Li/NH ₃	H ₂ , 1 MOLE	TRANS-ALKENE $\begin{array}{c} H \quad H \\ \diagdown \diagup \\ R-C=C-R' \\ \diagup \diagdown \\ H \quad H \end{array}$	TRANS
INTERNAL ALKYNE $R-C\equiv CR'$	H ₂ /Pt OR Pd (2MOLES)	H ₂ , 2 MOLES	ALKANE RCH_2CH_2R'	NOT APPLICABLE

Table 111

Reagent code list for preparation
of alkyl halides

ORGANOHALIDES CODE LIST

STARTING MATERIAL	REAGENT CODE	MECHANISM	PRODUCT	USES
Alkene	HCl HBr, HI	Carbocation	Markonikov	Preparation of Alkyl Halide
Alkene	Cl ₂ /light, Br ₂ /light	Free Radical	R-Cl, R-Br	Preparation of Alkyl Halide Cl ₂ not selective Br ₂ selective
Alkene	NBS	Free Radical	R-Br	Allylic Bromination Unless Alkene Symmetrical Product Mixture
Alkene	Cl ₂ /CCl ₄ , Br ₂ /CCl ₄	Cyclic Br ⁺ Cl ⁺	Trans dihalide	Preparation of Dihalide
ROH	HI, or HCl, or HBr	SN1 or SN2	RCl, RBr, RI	Reagents for SN1, SN2 displacements No Prim or sec alcohol
ROH	PBr ₃	Cyclic	RBr	Reagents for SN2 displacements No Tertiary alcohol
ROH	SOCl ₂	Cyclic	RCl	Reagents for SN2 displacements No Tertiary alcohol
ROH	Tosyl Chloride	DONT NEED	ROTS	Excellent leaving group for SN2 displacements No Tertiary alcohol
RX X = Halogen	Mg /ether or THF	DONT NEED	R-MgX	Preparation of Grignard Reagent Source of Strong base R ⁻
RX X = Halogen	Li /ether or THF	DONT NEED	R-Li	Preparation of Organolithium Compound Source of Strong base R ⁻
RLi	CuI	DONT NEED	(R) ₂ CuLi	Preparation of Gilman Reagent
RX X = Halogen	(R') ₂ CuLi	DONT NEED	R-R'	Coupling of alkyl or aryl groups, Gilman Reagent Source of Strong base R ⁻
R-Mg-X X = Halogen	HOH or DOD	DONT NEED	R-H OR R-D	Alkane synthesis, isotopically labeled alkanes

Table IV

Reagent code list for reactions
of alkyl halides

<u>REACTIONS</u>	<u>OF ALKYL</u>	<u>HALIDES</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING</u> <u>MATERIAL</u> 1° OR 2° alkyl halide	<u>REAGENT</u> <u>CODE</u> Nucleophile	<u>MECHANISM</u> SN2	<u>PRODUCT</u> Substitution	<u>STEREOCHEMISTRY</u> Inversion
3° alkyl halide	Nucleophile	SN1	Substitution	Racemization
1° OR 2° alkyl halide	Nucleophile with heat	E2	Alkene	<u>Trans-Coplanar</u> for H and Halide Usually gives <u>most substituted</u> alkene unless trans coplanar arrangement cannot result in most substituted alkene
3° alkyl halide	Nucleophile with heat	E1	Alkene	Carbocation intermediate Always gives <u>most substituted</u> <u>alkene</u>

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Table V

Reagent code list for reactions
of aromatic compounds

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REACTIONS OFAROMATICSCODELISTAr = C₆H₅EAS =ElectrophilicAromaticSubstitutionNAS =NucleophilicAromaticSubstitution

<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>ACTIVE SPECIES</u>	<u>MECHANISM</u>	<u>PRODUCT</u>	<u>USES</u>	<u>LIMITATIONS</u>
Ar-H	Br ₂ /FeBr ₃	Br ⁺	EAS	Ar-Br	Halogenation	None
Ar-H	Cl ₂ /FeBr ₃	Cl ⁺	EAS	Ar-Cl	Halogenation	None
Ar-H	I ₂ /HNO ₃	I ⁺	EAS	Ar-I	Halogenation	None
Ar-H	HNO ₃ /H ₂ SO ₄	NO ₂ ⁺	EAS	ArNO ₂	Nitration	None
Ar-H	H ₂ SO ₄	HSO ₃ ⁺	EAS	ArSO ₃ H	Sulfonation	None
Ar-H	RCI or RBr/ AlCl ₃	R ⁺ R cannot be Ar or H ₂ C=CH-	EAS	Ar-R	Alkylation	Carbocation Rearranges
Ar-H	RCOCl	RCO ⁺	EAS	ArCOR	Acylation	None
ArCOR	Zn/HCl H ₂ /Pt	H ₂	Reduction	ArCH ₂ R	Aryl ketone reduction	None
ArCH ₃	NBS	Br [•]	Free radical halogenation	ArCH ₂ Br	Allylic halogenation	None
ArNO ₂	Fe/HCl or Zn/HCl or H ₂ /Pd	H ₂	Reduction	ArNH ₂	Nitro reduction	None
ArCH ₃ OR	Na ₂ Cr ₂ O ₇ /H ⁺ KMnO ₄ /H ⁺	O	Oxidation	ArCOOH	Side Chain Oxidation	None
ArCH ₂ R	Na ₂ Cr ₂ O ₇ /H ⁺ KMnO ₄ /H ⁺	O	Oxidation	ArCOOH	Side Chain Oxidation	None
ArCH=CH ₂	H ₂ /Pt	H ₂	Reduction	ArCH ₂ CH ₃	Regular double bond reduced <u>aromatics no</u>	None
Ar(NO ₂) ₃ Cl	Nu: ⁻ Nu: ⁻ = OH ⁻ or <u>other nucleophile</u>	Nu: ⁻	Substitution NAS	Ar(NO ₂) ₃ Nu	Need Nitro or other electron withdrawing groups	

Table V1

Reagent code list for preparation and reactions
of alcohols

REACTIONS OF ALCOHOLS **CODE** **LIST**

<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>Reactive Species</u>	<u>PRODUCT</u>	<u>STRUCTURE</u>
ROH	NaH or NaNH ₂	H ⁻ or NH ₂ ⁻	Alkoxide Salt	RO ⁻ Na ⁺
1° Alcohol RCH ₂ OH	Dichromate or Permanganate/acid	O	Acid	RCOOH
2° Alcohol RCHOHR'	Dichromate or Permanganate/acid	O	Ketone	RCOR'
Alkene	Borane/peroxide	HOH	Alcohol	Anti-Markonikov, cis
Alkene	Hg salt/water	HOH	Alcohol	Markonikov
Alkene	OSO ₄	O	diol	cis diol
H ₂ C=O	NaBH ₄	H-	Primary alcohol	CH ₃ OH
H ₂ C=O	LiAlH ₄	H-	Primary alcohol	CH ₃ OH
RCH=O(aldehyde)	NaBH ₄	H-	Primary alcohol	RCH ₂ OH
RCH=O(aldehyde)	LiAlH ₄	H-	Primary alcohol	RCH ₂ OH
RCH=O(aldehyde)	R'MgBr	R-	Sec Alcohol	RR'CHOH
RC=OR' (ketone)	R''MgBr	R-	Tert Alcohol	RR'R''OH
RC=OR' (ketone)	NaBH ₄	H-	Sec Alcohol	RR'CHOH
RC=OR' (ketone)	LiAlH ₄	H-	Sec Alcohol	RR'CHOH
RC=OOR (ester)	NaBH ₄	H-	NR	
RC=OOR (ester)	R'MgBr (2 moles)	R-	Tert Alcohol	RR'R'OH
RC=OOR (ester)	LiAlH ₄	H-	Primary alcohol	RCH ₂ OH
RCOOH, acid	NaBH ₄	H-	NR	
RCOOH, acid	LiAlH ₄	H-	Primary alcohol	RCH ₂ OH
3° Alcohol	HX X = halide	Carbocation	Halide	RX

2° or 1° Alcohol	PBr ₃ or SOCl ₂	SN2	Halide	RBr or RCl
ROH	TsCl	ROTs	Tosylate	good leaving group
ROH	Acid or POCl ₃	Carbocation	Alkene	Zaitsev Product
ROH	R'COOH/acid	ROH	Ester	RCOOR'
1° Alcohol RCH ₂ OH	PCC	O	Aldehyde	RCH=O
2° Alcohol RCHOHR'	PCC	O	Ketone	RCOR'

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Table VII

Reagent code list for preparation and reactions
of ethers, epoxides, thiols and sulfides

<u>REACTIONS</u>	<u>OF ETHERS</u>	<u>THIOLS OR</u>	<u>SULFIDES</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>Reactive Species</u>	<u>PRODUCT</u>	<u>STRUCTURE</u>	<u>Limitation</u>
RBr	NaOR	RO ⁻	ETHER	ROR'	R not 3°
ROH	CH ₃ I/Ag ₂ O	CH ₃ I	Methyl Ether	ROCH ₃	None
Alkene	1) Hg salt, R'OH 2) NaBH ₄	R'OH	ETHER	ROR'	Markonikov Addition R'OH
Ether, ROR'	HX, H=Halogen	HX	Alcohol + Halide	ROH + R'X	If R and R' = 1° or 2° X attacks less hindered <u>if 3° X attacks 3°</u>
Allyl Phenyl Ether	Heat, Rearranges	Concerted	o-allyl phenol	o-allyl phenol	None
Alkene	Peracid RCOOOH	O	Epoxide	Cis addition	None
Halohydrin	Base	Alkoxide	Epoxide	Cis epoxide	None
Epoxide	H ₂ O	H ₂ O	1,2 diol	Trans	None
Epoxide	HX, H=Halogen	HX	Halohydrin		If R and R' = 1° or 2° X attacks less hindered <u>if 3°, X attacks 3°</u>
Epoxide	Base	HO ⁻	Diol	Trans	HO ⁻ attacks less hindered side
Ethylene Oxide	RMgBr	R ⁻	Alcohol	RCH ₂ CH ₂ OH	None

<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>Reactive Species</u>	<u>PRODUCT</u>	<u>STRUCTURE</u>	<u>Limitation</u>
RX X= halogen	NaSH	HS-	Thiol	RSH	low yield
RX X= halogen	Thiourea	Thiourea	Thiol	RSH	none
RSH	I ₂ or peroxide	O	disulfide	RSSR	none
RX X= halogen	NaSR'	RS-	sulfide	RSR'	R no 3° SN2
RSR'	Peroxide	O	Sulfoxide	RS=OR'	none
RS=OR'	Peracid	O	Sulfone	RSO ₂ R'	none

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Table VIII

Reagent code list for preparation and reactions
of aldehydes and ketones

<u>ALDEHYDES</u>	<u>AND</u>	<u>KETONES</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING MATERIAL</u>	<u>CODE</u>	<u>REACTIVE SPECIES</u>	<u>PRODUCT</u>	<u>MECHANISM</u>
1° Alcohol	PCC	O	aldehyde	N/A
Ester	DIBALH	H ⁻	Aldehyde	H ⁻ Attack on C=O
Acid Chloride	R ₂ CuLi	R ⁻	Ketone	R ⁻ Attack on C=O
Aldehyde	CrO ₃ or other strong O agent	O	Acid	N/A
Aldehyde or Ketone	NaBH ₄ or LAH	H ⁻	Alcohol	H ⁻ Attack on C=O
Aldehyde or Ketone	RMgBr	R ⁻	Alcohol	R ⁻ Attack on C=O
Aldehyde or Ketone	HCN	CN ⁻	Cyanohydrin	CN ⁻ Attack on C=O
Aldehyde or Ketone	RNH ₂	NH ₂	Imines	RNH ₂ Attack on C=O
Aldehyde or Ketone	2° Amine R ₂ NH	R ₂ NH	Enamine	R ₂ NH Attack on C=O
Aldehyde or Ketone	H ₂ NNH ₂ /Base	H ₂ NNH ₂	Hydrocarbon	H ₂ NNH ₂ attack on C=O
Aldehyde or Ketone	ROH 1 mole	ROH	Hemiacetal	ROH Attack on C=O
Aldehyde or Ketone	ROH 2 moles	ROH	Acetal	ROH Attack on Hemiacetal
Aldehyde or Ketone	Wittig Reagent	Wittig Reagent	Alkene	Wittig attack on C=O
Alpha-Beta Unsaturated Aldehyde or Ketone	Nu ⁻	Nu ⁻	Beta adduct	Nu ⁻ attack on C=C

ALKENE	O_3	O	Aldehyde or Ketone	O Cleaves C=C
Aromatic	Acyl Chloride/ Aluminum chloride	RCO+	Aryl Ketone	RCO + Attacks Ring
Terminal Alkyne	Hg Salt/HOH/ NaBH ₄	HOH	Methyl Ketone	HOH adds Markonikov
Aldehyde or Ketone	HOH	HOH	1,1 diol	HOH attacks C=O

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Table IX

Reagent code list for preparation and reactions
of carboxylic acids

<u>PREPARATION</u>	<u>AND REACTIONS OF</u>	<u>CARBOXYLIC</u>	<u>ACIDS</u>	<u>CODE LIST</u>
<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>Active Species</u>	<u>PRODUCT</u>	<u>LIMITATION</u>
Acids RCOOH	OH ⁻	OH ⁻	Salts, RCOONa	
Salts, RCOONa	R'X	RCOO ⁻	Esters RCOOR'	SN ₂ No 3°
Acids RCOOH	R'OH	R'OH	Esters RCOOR'	
Acids RCOOH	LAH	H ⁻	1° Alcohols RCH ₂ OH	
Acids RCOOH	SOCl ₂	SOCl ₂	Acid Chlorides RCOCl	
Acid Chlorides RCOCl	R'OH	R'OH	Esters RCOOR'	
Acid Chlorides RCOCl	NH ₃	NH ₃	Amides, RCONH ₂	
Alkyl Benzenes	KMNO ₄ /H ⁺ Or CrO ₃	O	Benzoic acids ArCOOH	
Alkenes	KMNO ₄ /H ⁺ Or CrO ₃	O	Carboxylic acids RCOOH	
1° Alcohols	KMNO ₄ /H ⁺ Or CrO ₃	O	Carboxylic acids RCOOH	
Aldehydes	KMNO ₄ /H ⁺ Or CrO ₃	O	Carboxylic acids RCOOH	
RX X = Hal or OTS	CN ⁻	CN ⁻	Nitriles RCN	SN ₂ No 3°
Nitriles RCN	H ₃ O ⁺ Full Hydrolysis	H ₃ O ⁺	Carboxylic acids RCOOH	
Nitriles RCN	H ₃ O ⁺ Partial Hydrolysis	H ₃ O ⁺	Amides RCONH ₂	
Grignards RMgBr	1) CO ₂	R ⁻	Carboxylic acids	

Amides, RCONH_2	POCl_3 Dehydrate	POCl_3	Nitriles RCN
Amides, RCONH_2	H_3O^+ Hydrolysis	H_3O^+	Carboxylic acids RCOOH
Nitrile RCN	LAH	H^-	1° Amines RCH_2NH_2
Amides, RCONH_2	LAH	H^-	1° Amines RCH_2NH_2
Nitriles RCN	1) Grignard R'MgBr 2) H_3O^+ Hydrolysis	R^-	Ketones RCOR'

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Table X

Reagent code list for preparation and reactions
of carboxylic acid chlorides, esters, anhydrides
and amides

PREPARATION AND REACTIONS OF CARBOXYLIC ACID DERIVATIVES CODE LIST

NU = NUCLEOPHILE

<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>NU</u>	<u>PRODUCT</u>
ACID RCOOH	SOCl ₂	NA	ROCl
RCOOH	P ₂ O ₅ dehydrate	NA	RCOOCOR anhydride
RCOO ⁻ Na ⁺ ACID SALT	R'X R = 1°	RCOO ⁻	RCOOR' ESTER
RCOOH	R'OH	R'OH	RCOOR' ESTER
RCOCl ACID CHLORIDE	R'OH	R'OH	RCOOR' ESTER
RCOCl	R'COO ⁻ Na ⁺	RCOO ⁻	RCOOCOR' anhydride
RCOCl	H ₂ O	H ₂ O	RCOOH ACID
RCOCl	R'NH ₂	NH ₂	RCONHR' 2° AMIDE
RCOCl	RR''NH	NH	RCONR'R'' 3° AMIDE
RCOCl	NH ₃	NH ₃	RCONH ₂ AMIDE
RCOCl	DIBALH	H ⁻	RCOH ALDEHYDE
RCOCl	LAH	H ⁻	RCH ₂ OH 1° ALCOHOL
RCOCl	RMgBr	R ⁻	RR'R'COH 3° ALCOHOL

RCOOR' ESTER	H ₂ O	H ₂ O	RCOOH ACID
RCOOR'	OH-	OH-	R'COO- Na+ ACID SALT
RCOOR'	NH ₃	NH ₃	RCONH ₂ AMIDE
RCOOR'	R'NH ₂	NH ₂	RCONHR' 2° AMIDE
RCOOR'	RR''NH	NH	RCONR'R'' 3° AMIDE
RCOOR'	DIBAH	H-	RCOH ALDEHYDE
RCOOR'	LAH	H-	RCH ₂ OH 1° ALCOHOL
RCOOR'	R''MgBr 2 MOLES	R-	RR''R''COH 3° ALCOHOL
RCONH ₂ AMIDE	POCl ₃ DEHYDRATE	NA	RCN NITRILE
RCONH ₂	LAH	H-	RCH ₂ NH ₂ 1° AMINE
RCONH ₂	H ₃ O+ HEAT	H ₂ O	RCOOH ACID
RCONH ₂	OH-	OH-	R'COO- Na+ ACID SALT
RCONHR' 2° AMIDE	LAH	H-	RCH ₂ NHR' 2° AMINE
RCONR'R'' 3° AMIDE	LAH	H-	RCH ₂ NRR'' 3° AMINE
RCN NITRILE	LAH	H-	RCH ₂ NH ₂ 1° AMINE
RCN	H ₃ O+	H ₂ O	RCOOH

RCN

OH-

OH-

R'COO- Na+
ACID SALT

RCN

1) R'MgBr
2) H₃O+

R-

RCOR'
KETONE

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Table XI

Reagent code list for carbonyl

alpha-substitution reactions

<u>CARBONYL ALPHA</u>	<u>SUBSTITUTION</u>	<u>REACTIONS</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>NU⁻</u>	<u>PRODUCT</u>	<u>STRUCTURE</u>
Aldehyde or ketone with alpha hydrogens $RCH_2C=O(H)(R)$	X_2/H^+ $X = Cl_2 \text{ or } Br_2 \text{ or } I_2$	Enol	alpha halo aldehyde or ketone	$XCH_2C=O(H)(R)$ $X = \text{halogen}$
Aldehyde or ketone with alpha hydrogens $RCH_2C=O(H)(R)$	X_2/OH^- $X = Cl_2 \text{ or } Br_2 \text{ or } I_2$	Enolate $RCH^{\cdot}C=O(H)(R)$	alpha di-halo aldehyde or ketone brominates two times	$X_2CC=O(H)(R)$ $X = \text{halogen}$
Methyl ketone $R-COCH_3$	X_2/OH^- $X = Cl_2 \text{ or } Br_2 \text{ or } I_2$	Enolate $R-COCH_2^{\cdot}$	Acid brominates three times	$RCOOH$ <u>Haloform Reaction</u>
Acid with alpha Hydrogens RCH_2COOH	1) PBr_3/Br_2 2) H^+	Enol	alpha-halo acid	<u>Hell Volhard Zelinsky reaction</u> $RCHBrCOOH$
alpha halo aldehyde or ketone $RCH_2CHXCOR' \quad X=Hal$	Amine/heat Dehydro halogenate	NA	alpha-beta unsaturated aldehyde/ketone	$RCH=CHCOR'$
Aldehyde or ketone or ester or nitrile with alpha hydrogens $RCH_2C=O(H)(R)$	1) LDA 2) $R'X$ $X = \text{halogen}$ SN2	Enolate $RCH^{\cdot}C=O(H)(R)$	alpha-alkylated product	$RR'CHC=O(H)(R)$
Malonic ester $CH_3CH_2OCOCH_2COOCH_2CH_3$	1) Base, $OR^{\cdot}$ 2) $R'X$, SN2 3) H^+ lose CO_2	Enolate	Acid	$R'CH_2COOH$
Acetoacetic ester $CH_3COCH_2COOCH_2CH_3$	1) Base, $OR^{\cdot}$ 2) $R'X$, SN2 3) H^+ lose CO_2	Enolate	Methyl Ketone	CH_3COCH_2R'

Table XII

Reagent code list for carbonyl
condensation reactions

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<u>CARBONYL</u>	<u>CONDENSATION</u>	<u>REACTIONS</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>NU⁻</u>	<u>PRODUCT</u>	<u>STRUCTURE</u>
Aldehyde or ketone with alpha hydrogens $R-COCH_3$	1) Base, OR ⁻ self condensation <u>two moles</u>	Enolate $R-COCH_2^{\cdot-}$	beta-hydroxy ketone $RCOCH_2CCH_3$ may lose H_2O to give alkene $RCOC=CCH_3$	<u>Aldol Condensation</u>
<u>MIXED ALDOL POSSIBLE IF</u>	<u>ONE ALDEHYDE OR</u>	<u>KETONE HAS</u>	<u>NO ALPHA</u>	<u>HYDROGENS</u>
<u>IF BOTH IN</u>	<u>SAME MOLECULE A</u>	<u>CYCLIC</u>	<u>beta-hydroxy ketone</u>	<u>RESULTS</u>
Ester with Alpha Hydrogens CH_3COOCH_3	1) Base, OR ⁻ self condensation <u>two moles</u>	Enolate $CH_2^{\cdot-}COOCH_3$	beta-keto ester	<u>Claisen Condensation</u> $CH_3COCH_2COOCH_3$
<u>MIXED CLAISEN POSSIBLE IF</u>	<u>ONE ESTER</u>	<u>HAS</u>	<u>NO ALPHA</u>	<u>HYDROGENS</u>
<u>IF BOTH IN</u>	<u>SAME MOLECULE A</u>	<u>CYCLIC</u>	<u>BETA DIKETONE</u>	<u>RESULTS</u>
$H_2C=CH-C=O(H)(R)$ alpha, beta unsat ketone	beta diketone $RCOCH_2COCH_3$ / OR-	Enolate $RCOCH^{\cdot-}COCH_3$		<u>Michael Reaction</u> $NUCH_2CH_2C=O(H)R$ $NU= RCOCH^{\cdot-}COCH_3$ Congugate addition
$H_2C=CH-C=O(H)(R)$ alpha, beta unsat ketone	1) Enamine	Enolate		$RCOCH_2CH_2C=O(H)(R)$ Stork Modification of Michael Reaction Congugate addition

Table XIII

Reagent code list for preparation
and reactions of amines

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<u>PREPARATION AND</u>	<u>REACTIONS</u>	<u>OF</u>	<u>AMINES</u>	<u>CODE</u>	<u>LIST</u>
<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>MECHANISM</u>	<u>PRODUCT</u>	<u>USES</u>	<u>LIMITATIONS</u>
Nitrile RCN	LAH	H- Reduction	RCH_2NH_2	1° Amine Prep	None
Amide RCONH_2	LAH	H- Reduction	RCH_2NH_2	1° Amine Prep	None
Primary Alkyl Halide RCH_2Br	NH_3	SN_2	Primary Amine RCH_2NH_2	Bulk preparation of amines	Gives mixtures with sec, tert amines
Primary Amine RCH_2NH_2	Primary Alkyl Halide RCH_2Br	SN_2	Sec Amine $(\text{RCH}_2)_2\text{NH}$	Bulk preparation of amine	Gives mixtures with tert amines
Sec Amine $(\text{RCH}_2)_2\text{NH}$	Primary Alkyl Halide RCH_2Br	SN_2	Tert Amine $(\text{RCH}_2)_3\text{N}$	Bulk preparation of amine	Gives mixtures with quat amines
Tert Amine $(\text{RCH}_2)_3\text{N}$	Primary Alkyl Halide RCH_2Br	SN_2	"Quat" Amine $(\text{RCH}_2)_4\text{N}^+\text{Br}^-$	Bulk preparation of Soaps	None
Phthalamide	Primary Alkyl Halide RCH_2Br	SN_2	Primary Amine RCH_2NH_2	Prep primary amine no sec or tert byproduct	No sec or tert halide
Primary Alkyl Halide RCH_2Br	Sodium Azide NaN_3	SN_2	Primary Alkyl Azide RCH_2N_3	Reactive Synthetic intermediate	Must be Primary Halide
Primary Alkyl Azide RCH_2N_3	H_2/Pd or LAH	Reduction	Primary Amine RCH_2NH_2	High yields of Primary amine	None
Aldehyde/ketone $\text{RCH}_2\text{CHOH(R)}$	1, NH_3 2) LAH	Reduction	Prim or sec Amine	High yields of amine	None
Amide RCONH_2	1) OH^- Br_2	Isocyanate Intermediate	Primary Amine RNH_2	Amine with one less carbon	None Hoffman <u>Degradation</u>
Acid Chloride RCOCl	1) NaN_3 2) Heat $-\text{CO}_2$	Isocyanate Intermediate	Primary Amine RNH_2	Amine with one less carbon	None Curtius <u>Rearrangement</u>

ArNH ₂ Aromatic Amine	HONO Nitrous acid		ArN ₂ ⁺ Diazonium salt	Source of Ar ⁺	None
ArN ₂ ⁺ Diazonium salt	HX CuX X= hal	X ⁻ on Ar ⁺	ArCl or ArBr or ArI	Prep Halobenzenes	None
ArN ₂ ⁺	CuCN	CN ⁻ on Ar ⁺	ArCN	Prep Aromatic Nitriles	None
ArN ₂ ⁺	Cu ₂ O/H ₂ O	OH ⁻ on Ar ⁺	ArOH	Prep Phenols	None
ArN ₂ ⁺	H ₃ PO ₂	H ⁻ on Ar ⁺	ArH	Replace NO ₂ on Ring with H	None
"Quat" Amine RCH ₂ CH ₂ N(CH ₃) ₃ ⁺ Br ⁻	1) Ag ₂ O or OH- 2) Heat loses (CH ₃) ₃ N	E2	Alkene RCH=CH ₂	Gives <u>least</u> substituted alkene <u>Hoffman Elimination</u>	None

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Table XIV

Reagent code list for
reactions of carbohydrates

<u>REACTIONS</u>	<u>OF</u>	<u>SUGARS</u>	<u>CODE</u>	<u>LIST</u>	
<u>STARTING MATERIAL</u>	<u>REAGENT CODE</u>	<u>MECHANISM</u>	<u>PRODUCT</u>	<u>USES</u>	<u>COMMENTS</u>
KETO SUGAR D OR L	<u>OH⁻</u>	<u>enolization</u>	ALDO SUGAR	SUGAR ISOMERIZATION	KETO SUGAR GIVES <u>POSITIVE TOLLENS</u> TEST DUE TO THIS!
ANY ALDO OR KETO SUGAR	NaBH ₄	Hydride reduction	polyol	SUGAR REDUCTION	
ANY ALDO OR KETO SUGAR	Ag ⁺ (NH ₃) ₂ OH ⁻ <u>Tollens reagent</u>	Oxidation	Acid Sugar and Ag metal COOH on Terminal of Sugar	SUGAR OXIDATION	<u>Silver mirror</u> means reducing sugar with a hemiacetal or free aldehyde group <u>TEST FOR GLUCOSE!</u>
ALDO SUGAR	Cu ²⁺ (NH ₃) ₄ <u>Blue Fehlings</u> <u>Solution</u>	Oxidation	Acid Sugar and Cu ₂ O COOH on Terminal of Sugar	SUGAR OXIDATION	<u>Red Cu₂O</u> means reducing sugar with hemiacetal or free aldehyde group <u>TEST FOR GLUCOSE!</u>
ALDO SUGAR	Br ₂	Oxidation	Acid Sugar COOH on Terminal of Linear Sugar	SUGAR OXIDATION	
ALDO SUGAR	HNO ₃	Oxidation	Acid Sugar COOH on Terminal of Linear Sugar	SUGAR OXIDATION	
ALDO SUGAR	1) HCN 2) H ₂ / BaSO ₄ 3) H ₃ O ⁺	Cyanohydrin then hydrolysis	ALDO SUGAR WITH ONE MORE CARBON	SUGAR SYNTHESIS	New sugar mixture of enantiomers at newly created site <u>Kiliani-Fischer</u> <u>Synthesis</u>
ALDO SUGAR	1) NH ₂ OH 2) Ac ₂ O 3) OH ⁻	Oxime then dehydration to cyanohydrin	ALDO SUGAR WITH ONE LESS CARBON	SUGAR SYNTHESIS	<u>Wohl Degradation</u>

Alpha (Axial) cyclic sugar	OH ⁻ or H ₃ O ⁺	Ring opening to free aldehyde	Beta (equatorial) cyclic sugar (predominates)	CYCLIC ISOMERIZATION TO MOST STABLE FORM	<u>MUTAROTATION</u>
Alpha or Beta cyclic sugar	ROH/H ₃ O ⁺	Ether formation at anomeric carbon	<u>Glycoside</u> RO at anomeric carbon	<u>Protects sugar from</u> <u>mutarotation</u> Not reversible to hemiacetal at anomeric carbon	<u>Negative Tollens</u> <u>Test!</u> No aldehyde present
Sucrose or other cyclic sugar with no hemiacetal carbon	Ag ⁺ NH ₃ OH ⁻ <u>Tollens reagent</u> or Cu ⁺² (NH ₃) ₄ <u>Blue Fehlings</u> <u>Solution</u>	NONE!	NR		Nothing to Oxidize

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