Haloalkanes, Haloarenes

Reagent	Condition	Reactant	Product	Byproduct	Comment
Prep of haloalkanes					
Cl2	diffused sunlight/UV light /high Temp	Alkane	Alkyl Chloride	HCl	reaction continues till all H are replaced by Cl, not suitable method to get single product
Br2	Anhydrous AlBr3	Alkane	Alkyl Bromide		reaction continues till all H are replaced by Br, not suitable method to get single product
I2		Alkane	Alkyl Iodide	HI	Reversible reaction as HI is strong reducing agent. Hence to prevent reverse reaction , oxidising agents are required that decompose HI
I2	HIO3/HgO/HNO3	Alkane	Alkyl Iodide	H2O/HgI2 & H2O /NH3 & H2O	Iodination stops at monoiodo stage
F2		Alkane	Alkyl Fluoride	HF	explosive reaction, HF poisonous and corrosive

HI/HBr/HCl		Symmetrical Alkene	alkyl halide		order of reactivity HI>HBr>HCl
HI/HBr/HCl		Unsymmetrical alkene	secondary alkyl halide(major)	primary alkyl halide (minor)	Major product by **Markownikoff's rule** for unsymmetrical alkenes, shown mainly by HCl/HI
HBr	Na2O2..peroxide	Unsymmetrical alkene	primary alkyl halide (major)	secondary alkyl halide(minor)	**antimarkownikoff's rule, Kharasch effect, Kharasch Mayo effect**/shown mainly by HBr
Lucas Reagent ConcHCl+ZnCl2	heat	alcohol	alkyl chloride	H2O	Primary and secondary alcohol require catalyst ZnCl2, tertiary alcohol does not , it reacts with only conc HCl
NaBr+H2SO4	Reflux	alcohol	alkyl bromide	H2O	conc H2SO4 for primary alcohol/dil H2SO4 for sec tert alcohol
HI	heat	alcohol	alkyl iodide	H2O	
NaI/KI	95% phosphoric acid	alcohol	alkyl iodide	H2O	reactivity of alcohols tert>sec>primary
PCl3	heat	alcohol	alkyl chloride	H3PO3	PCl3 stable/PBr3,PI3

					less stable
Red P+Br2 makes PBr3		alcohol	alkyl bromide	H3PO3	
Red P +I2 makes PI3		alcohol	alkyl iodide	H3PO3	
PCl5	reflux	alcohol	alkyl chloride	HCl+POCl3	PCl5 stable/PBr5,PI5 does not exist
SOCl2	reflux/ Pyridine	alcohol	alkyl chloride	SO2,HCl gases	best method as gases escape
NaI	Dry acetone	alkyl chloride/alkyl bromide	alkyl iodide	NaCl/NaBr get ppted	**Finkelstein reaction**
AgF/CoF2/SbF/Hg2F2		alkyl chloride/alkyl bromide	alkyl fluoride	metal chloride	**Swarts reaction**
Substitution reactions of haloalkanes					
aqueous alkali KOH/NaOH	boil	Alkyl halide	alcohol	metal halide	**SN2** for primary alkyl halide,bimolecular one step reaction , backside attack **SN1** for tert alkyl halide unimolecular two step reaction , both side attack possible
moist Ag2O behaves as AgOH	heat	Alkyl halide	alcohol	silver halide	

alcoholic soln of KCN	boil	Alkyl halide	alkyl cyanide	metal halide	one C increases / in strong base CN attacks through C
AgCN	heat	alkyl halide	alkyl isocyanide	silver halide	CN attacks through nitrogen
alcoholic NH3 in excess	pressure	alkyl halide	alkyl amine	HX	mix of prim,sec,tert,quat mines formed **Hoffmann's ammonolysis**
Na		alcohol	sodium alkoxide	H2	
sodium alkoxide		alkyl halide	ether	sodium halide	**Williamson's synthesis of ethers**
Ag salt of carboxylic acid		alkyl halide	alkyl carboxylate ester	silver halide	
		alkyl halide			
		alkyl halide			
		alkyl halide			
Reagent	Condition	Reactant	Product	Byproduct	Comment
Elimination reactions of Haloalkanes					
alcoholic soln of NaOH/KOH		alkyl halide with beta hydrogen	alkene	metal halide + H2O	**Saytzeff rule** : if two or more beta hydrogen then alkene with more no of alkyl groups to c atom is formed/H from c atom with least no of H atoms is

					removed.
Na	Dry ether	alkyl halide	alkane	sodium halide	**Wurtz reaction ; formation of higher alkane ,** self coupling and cross coupling alknes mixtures are formed
Pure dry Mg	pur dry ether	alkyl halide	**alkyl magnesium halide**		**Grignard reagent :** (metal bonded to C is organometallic compound)highly reactive, reacts with H2),amines,alcohols so reactions are carried under dry conditions
Grignard reagent	H2O	alkane	Mg(OH)X		
Preparation of Haloarenes					
Cl2/Br2	Lewis acid like FeCl3,BCl3, Fe as catalyst /dark	toluene	o halo and p halo toluene	HCl	electrophilic substitution , with I reaction is reversible hence oxidising agent required, F …highly reactive ,

					fluoro compounds can not be prepared
NaNO2/HCl	heat,	aniline	benzene diazonium chloride		**Sandmeyer reaction**
Cu2X2/CuX..HX X=Cl/Br…… or KI		benzene diazonium chloride	Haloarene	N2 / N2+KCl	
Nucleophilic substitution of Haloarenes					
NaOH	623K,pressure/ H+	chlorobenzene	phenol	Cl-	aryl halide less reactive towards Nucleophilic substitution so high temp pressure required
NaCN + CuCN	473k , pressure	chlorobenzene	Cyanobenzene	Cl-	
NH3, Cu2O	473k , pressure	chlorobenzene	aniline	CuCl+H2O	
NaOH		o or p nitro chlorobenzene	o or p notrophenol	Cl-	nucleophilic substitution is easy if e withdrawing group NO2 is at o or p position/2NO2 groups /3 NO2 groups : **picric acid (2,4,6 trinitrophenol)**

Electrophilic substitution of Haloarenes					
Cl2	anhydrous FeCl3	chlorobenzene	1,2minor, 1,4 major dichlorobenzene	HCl	halogenation
HNO3	Conc H2SO4 heat	chlorobenzene	1 chloro 4 nitro major benzene,1chloro 2 nitro minor benzene	H2O	nitration
Conc H2SO4	heat		4 chlorobenzene sulphonic acid major, 2 chlorobenzene sulphonic acid minor		sulphonation
methyl chloride	anhydrous AlCl3	chlorobenzene	4 chlorotoluene major/1 chloro minor	HCl	**Friedal craft's reaction alkylation**
Acetyl chloride	anhydrous AlCl3	chlorobenzene	pchloroacetophenone major o chloro minor	HCl	**Friedal craft's reaction acetylation**
CH3Br, Na	dry ether	bromobenzene	toluene	NaBr	**Wurtz fittig/fittig reaction**
Na	dry ether	bromobenzene	diphenyl	NaBr	**Wurtz fittig/fittig reaction**
Na	dry ether	bromomethane	ethane	NaBr	**Wurtz fittig/fittig reaction**