Preparation of Alkyl Halides

Product		Type of Reaction (name)	Reaction Conditions	Selectivity (Regio- and / or Stereo-)
Halides	from alkenes	Electrophilic Addition	HX, organic solvent (anhydrous)	Markovnikov Addition
	from alkenes	Free Radical Addition	HBr, H_2O_2, hν	Anti-Markovnikov
	from alkanes	Free Radical Substitution	X_2, hν	benzylic > allylic > 3° > 2° > 1°
	from alkenes	Free Radical Substitution	NBS, hν (gives allylic bromides)	benzylic and allylic H's
	from alcohols	Substitution	HX, ether (anhydrous)	3° alcohols only
	from alcohols	Substitution	$SOCl_2$ (gives alkyl chlorides)	1° and 2° alcohols
	from alcohols	Substitution	PBr_3 (gives alkyl bromides)	1° and 2° alcohols
1,2-halides (vic-dihalide)	from alkenes	Electrophilic Addition	Cl_2, Br_2, I_2 in CCl_4 solvent	Anti Stereochemistry
1,1,2,2-tetrahaloalkanes	from alkynes	Electrophilic Addition	X_2 (excess), anhydrous	
1,1-dihaloalkane (gem-dihalide)	from alkynes	Electrophilic Addition	HX (excess), anhydrous	Markovnikov
vinyl halide	from alkynes	Electrophilic Addition	HX (1 equivalent), anhydrous	Markovnikov, trans-addition of H-X
1,2-Dihaloalkene	from alkynes	Electrophilic Addition	X_2 (1 equivalent), anhydrous	trans addition of X-X

Reactions of Alkyl Halides

Alkenes	from alkyl halides	Elimination of HX	Strong Base (NaOH or $NaNH_2$)
Alkynes	from 1,2-dihalides	Double Elimination of HX	$NaNH_2$, NH_3
Grignard Reagents	(R-MgX from R-X)		1°, 2°, 3°-Alkyl, vinyl or aryl halide and $Mg^{(0)}$ in THF or ether
Organolithium	(R-Li from R-X)		1°, 2°, 3°-Alkyl, vinyl or aryl halide and $Li^{(0)}$ in pentane
Cuprate (Gilman's Reagent)	(R_2CuLi from R-Li)		Organolithium + CuI in THF or ether
Organometallic Coupling		Substitution	Cuprate + alkyl halide to give an alkane Cuprate + vinyl halide to give a substituted alkene Cuprate + aryl halide to give a substituted arene

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