

METHODS FOR FUNCTIONAL GROUP PREPARATION

CHAPTERS 1-13

I. ALKYL HALIDES

- (a) HX addition to alkenes [Markovnikov (Section 8.2) and HBr anti-Markovnikov (Section 10.9)]
- (b) X₂ addition to alkenes (Section 8.12)
- (c) Radical halogenation
 - (i) X₂/light/heat for alkanes (Sections 10.3, 10.4, 10.5, 10.6)
 - (ii) *N*-Bromosuccinimide (NBS)/heat/light for allylic and benzylic substitution (Section 13.2B)
- (d) R—OH + SOCl₂ (with pyridine) → R—Cl + SO₂ + pyridinium hydrochloride (Section 11.9)
- (e) 3 R—OH + PBr₃ → 3 R—Br + P(OH)₃ (Section 11.9)
- (f) R—OH + HX → R—X + H₂O (Sections 11.7, 11.8)

II. ALCOHOLS

- (a) Markovnikov addition of H₂O with catalytic H⁺ (Section 8.5)
- (b) Markovnikov addition of H₂O via (i) Hg(OAc)₂, H₂O, THF; (ii) NaBH₄, OH⁻ (Section 8.6)
- (c) Anti-Markovnikov addition of H₂O via (i) BH₃:THF; (ii) OH⁻, H₂O₂ (Section 8.7)
- (d) OsO₄ addition to alkenes (syn) (Section 8.16)
- (e) (i) RCO₃H (peroxycarboxylic acids); (ii) H₃O⁺ (Section 11.15)
- (f) Cleavage of ethers with one molar equiv. HX (Section 11.12A)
- (g) Opening of epoxides by a nucleophile (Sections 11.14, 11.15)
- (h) Lithium aluminum hydride or sodium borohydride reduction of carbonyl compounds (Section 12.3)
- (i) Grignard reaction with aldehydes, ketones, and epoxides (Sections 12.7B, C, 12.8)
- (j) Cleavage of silyl ethers (Section 11.11E)

III. ALKENES

- (a) E2 Dehydrohalogenation (preferred over E1 for alkene synthesis) (Section 7.6)
- (b) Dehydration of alcohols (Section 7.7)

- (c) Hydrogenation of alkynes: *Z* by catalytic hydrogenation, *E* by dissolving metal reduction (Sections 7.15A, B)
- (d) Diels-Alder reaction (forms one new double bond with ring formation) (Section 13.11)

IV. ALKYNES

- (a) Alkylation of alkynide anions (Sections 7.12 and 8.21)
- (b) Double dehydrohalogenation of vicinal or geminal dihalides (Section 7.9)

V. CARBON—CARBON BONDS

- (a) Alkylation of alkynide anions (Section 7.12 and 8.21)
- (b) Organometallic addition to carbonyl compounds and epoxides (e.g., Grignard or RLi reactions) (Sections 12.7B, C, 12.8)
- (c) Diels-Alder reaction (Section 13.11)
- (d) Addition of alkenes to other alkenes (e.g., polymerization) (Section 10.10 and Special Topic A)
- (e) Addition of a carbene to an alkene (Section 8.15)

VI. ALDEHYDES

- (a) (i) O_3 ; (ii) Zn, HOAc with appropriate alkenes (Section 8.17B)
- (b) Pyridinium chlorochromate (PCC) oxidation of 1° alcohols (Section 12.4A)

VII. KETONES

- (a) (i) O_3 ; (ii) Zn, HOAc with appropriate alkenes (Section 8.17B)
- (b) $KMnO_4/OH^-$ cleavage of appropriate alkenes (Section 8.17A)
- (c) H_2CrO_4 oxidation of 2° alcohols (Section 12.4C)

VIII. CARBOXYLIC ACIDS

- (a) (i) $KMnO_4/OH^-$; (ii) H_3O^+ with 1° alcohols (Section 12.4B)
- (b) (i) O_3 ; (ii) HOAc with alkynes (Section 8.20)
- (c) (i) $KMnO_4/OH^-$, heat; (ii) H_3O^+ with alkynes and alkenes (Sections 8.20 and 8.17A)
- (d) H_2CrO_4 oxidation of 1° alcohols (Section 12.4D, E)