Summary of Alcohol Reactions, Ch. 11.

1 $R{-}OH + NaZ \overset{???}{\rightleftharpoons} R{-}ONa + HZ$

Acid-Base

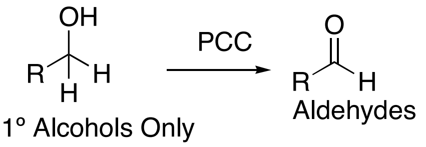
1. Deprotonation by a base.
2. Controlled by relative stability of $RO^{\ominus}$ versus $Z^{\ominus}$.
3. Consider relative electronegativity and whether either anion is resonance stabilized.

2 $R{-}OH \xrightarrow{Na} R{-}ONa$

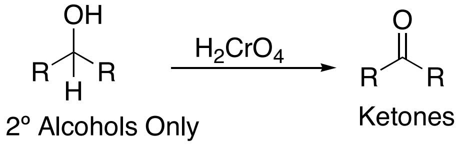
- Potassium (K) analogous.
- Key way to convert alcohol to alkoxide, reactive as S_N2 nucleophile and E2 base.

3 $R{-}OH \xrightarrow[2.\ R'{-}X]{1.\ Na} R{-}O{-}R'$

- Alkoxide formation-S_N2 route to ether
- The electrophile R'-X must be S_N2 reactive, preferably 1° with a good leaving group

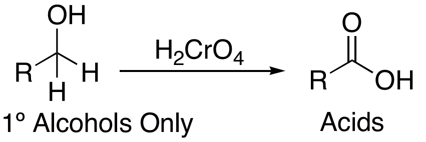
4 

- Key access to aldehydes, which are useful for more Grignard chemistry.
- Note difference between PCC and H_2CrO_4
- PCC does not react with 2° alcohols very rapidly

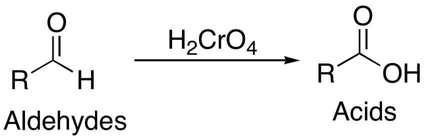
5 

$H_2CrO_4 = Na_2Cr_2O_7, H_2SO_4$ or CrO_3/H_2O

- Key access to ketones.
- PCC does not react very fast with 2° alcohols

6 

- Note difference between
- PCC and H_2CrO_4 when reacting with 1° alcohols.

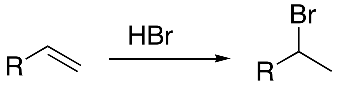
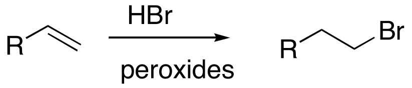
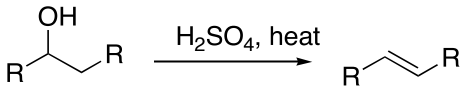
7 

8 $R{-}OH \xrightarrow{HBr} R{-}Br$

3° alcohols

Mech: Be able to draw!

- HI, HCl analogous
- Converts alcohol into a bromide that can be used in Grignards, E2 reactions
- Cation mechanism
- Usually not method of choice for 1°, 2° alcohols

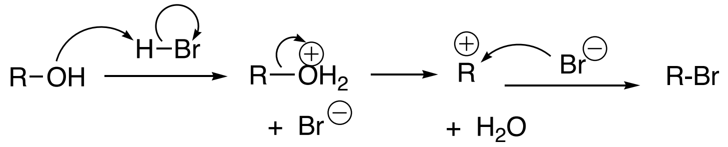
9	$R{-}OH \xrightarrow{PBr_3} R{-}Br$ 1° or 2° alcohols	- Converts alcohol into a bromide that can be used in Grignards, E2, S_N2 reactions - Inversion of stereochem - Not good for 3° alcohols
10	$R{-}OH \xrightarrow[\text{2. Mg}]{\text{1. } PBr_3 \text{ or HBr}} RMgBr$	- Quick 2-step conversion of alcohol into a nucleophilic Grignard
11	$R{-}OH \xrightarrow{P/I_2} R{-}I$ 1° or 2° alcohols	- Via PI_3
12	$R{-}OH \xrightarrow{SOCl_2} R{-}Cl$ 1° or 2° alcohols	- Retention of stereo!
13	$R{-}OH \xrightarrow[NEt_3]{TsCl} R{-}OTs$	- Tosylates are super leaving groups, better even than iodides. - Tosylates are well suited to S_N2 and E2 reactions.
14		- Markovnikov addition
15		- anti-Markovnikov addition
16	$R{-}H \xrightarrow{Br_2,\ hv} R{-}Br$	- Radical mechanism, 3° > 2° > 1°
17		- Zaytsev elimination

Mechanisms for ROH → RBr Reactions

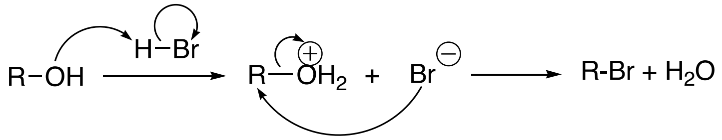
$$\underset{3^\circ}{\text{R-OH}} \xrightarrow{\text{HBr}} \text{R-Br}$$

3° mostly, sometimes 1°

HBr Mech for 3° ROH:



HBr Mech for 1° ROH:



$$\underset{1^\circ,\ 2^\circ}{\text{R-OH}} \xrightarrow{\text{PBr}_3} \text{R-Br}$$

1°, 2°

Mech: