Alcohols

(Review of Haloalkanes)

General & Naming.

Preparation

Properties

Reactions

Ref 11 : 1 – 10

Prob 11: 2, 4, 6, 7, 25, 26 a-e, 34

HMWK #05

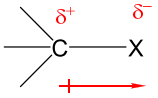
Adv Rdg 11 : 11 – 14

Haloalkanes Review

Naming: see Alkanes

Prep:
- radical halogenation of alkanes
- substitution at sp^3 C
- addition to alkenes/alkynes

Reactivity:
- based on polarization of C– X bond



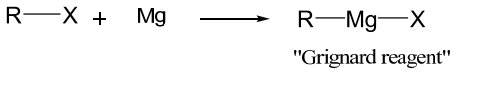
- empty σ* MO acts as e^- sink
- recall S_N2, E2

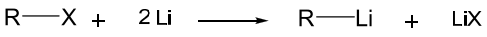
New Rxn

"haloalkanes can form organometallics"

esp. w/ Mg, Li

e.g.



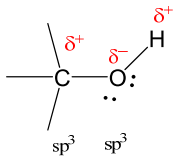


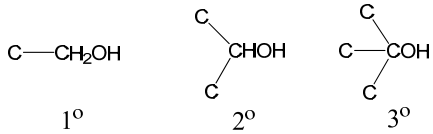
products act as R: $^-$

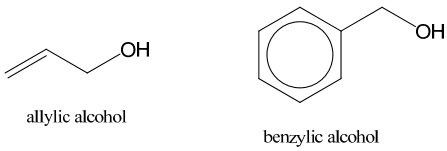
- very strong base (conj. base of very weak acid)
- very powerful in rxns w/ carbonyl cmpds

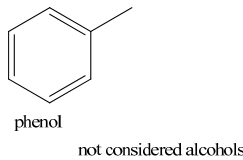
(*more in CHEM 263*)

Alcohols, General





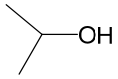




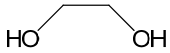
not considered alcohols

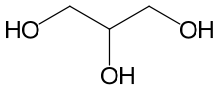
Some Common Names

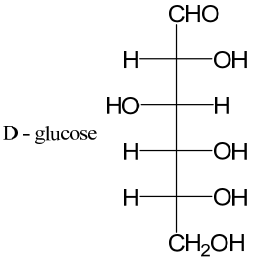
methyl hydrate CH_3OH

rubbing alcohol 

"alcohol" 

glycol 

glycerol 



D - glucose

table sugar, glucose dimer:

$C_{12}(H_2O)_{11}$

carbohydrates, such as
starch,
cellulose,
glycogen:

glucose polymers

Systematic Naming

1.) "ol" at the end (suffix)
(sometimes "hydroxy" as prefix)

2.) OH has higher priority than = , ≡ bonds

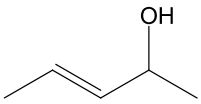
3.) find longest chain w/ OH

4.) give the C where it is attached
the lowest possible #

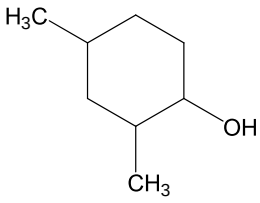
5.) multiple alcohols: -diol, -triol, ...

6.) if = , ≡ bonds present,
attachment # for alcohol is part of suffix

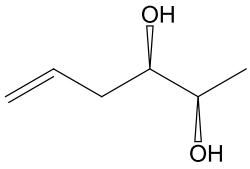
Practice



(3E) - 3 - penten - 2 - ol



2,4 - dimethylcyclohexanol



(2R, 3R) - 5 - hexen - 2,3 - diol

Prep.

A. from alkenes:

1.) direct hydration

2.) oxymercuration

3.) hydroboration

B. from haloalkanes

by S_N2 / S_N1 with OH^-

C. from carbonyl cmpds
(much more in CHEM 263)

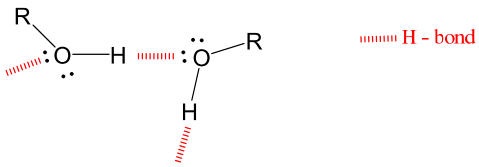
1.) by reduction

2.) by rxn w/ organometallics

H – Bonding

(“*strong dipole – dipole interaction*”)

Illustration:



Consequences

• intermolecular attraction ↑

(vapor pressure ↓ , b. p. ↑ , ...)

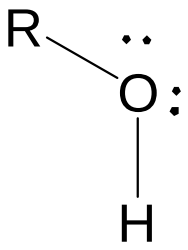
• important for “secondary structure (“folding”) of large biomolecules: carbohydrates,

protein

DNA

Basicity

Lewis Concept



• has lone pairs;

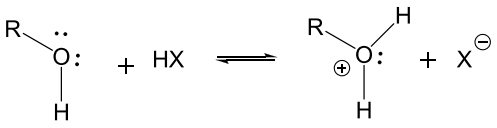
• is e^- donor

• acts as Lewis base

• can be nucleophilic reagent

Bronsted – Lowry Concept

base = H^+ acceptor



where HX could be: HCl, H_2SO_4, H_3O^+, HAc, NH_4+

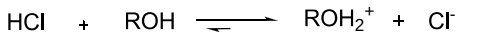
basicity

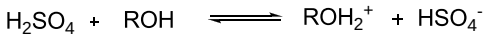
Use pK_a values to assess position of equil.

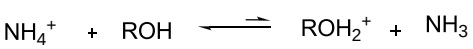
Illustration:

“acid”	pK_a
HCl	– 7
H_2SO_4	– 3
ROH_2^+	– 4
H_3O^+	– 4
NH_4^+	+ 9

Evaluation of equilibrium





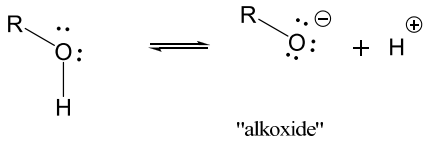


weaker acids are formed

Acidity

Bronsted – Lowry Concept

acid = H^+ donor



relevant pK_a’s

“acid”	pK_a
phenol	10
EtOH	16
MeOH	16
t-BuOH	18
H_2O	16

Rxns

1.) Alkoxide Form^n

2.) S & E Rxns

3.) Oxidation Rxns:

see CHEM 263

conversion to

aldehydes,

ketones,

acids

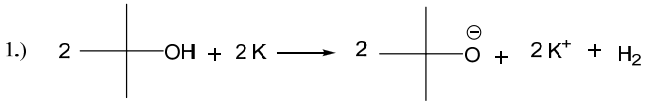
1. Alkoxide Form^n

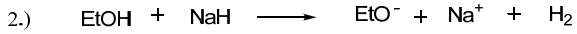
by trtmt with alkali metals (M•)

alkali metal Hydrides (MH)

(similar to rxns with H_2O

Examples

1.) 

2.) 

2.) Nucleophilic S & E Rxns

• OH a poor L.G. (being a strong base)

• no direct nucleophilic S & E rxns possible

∴ "activation needed"

A.) by protonation

B.) by making "active ester",

e.g., make tosylate

A.) "Oxonium Ion" Rxn

need strong mineral (inorganic) acid;

2 cases:

i.) no or poor nucleophile present

→ elimination

ii.) nucleophile present

→ substitution

"oxonium ion" rxn

i. with non-nucleophilic acid

(such as H_3PO_4, H_2SO_4, ...)

gives E products

(E1 or E2? depends on substrate structure!)

e.g., t - BuOH w/ $H_2SO_{4(aq)}$

"oxonium ion" rxn

i. with nucleophilic acid

(such as HCl(aq), HBr(aq), HI(aq) ...)

gives S products

Ex.

potential side rxn: formation of ether

B. "Active Ester" Method

i.) good base present → E rxn

e.g., trtmt of 1° / 2° alcohols w/

phosphorus oxychloride & pyridine gives E2 products

General example:

active ester method

i.) no base present → S rxn

e.g., trtmt of 1° / 2° alcohols w/

thionyl chloride gives S_N2 products

Example: