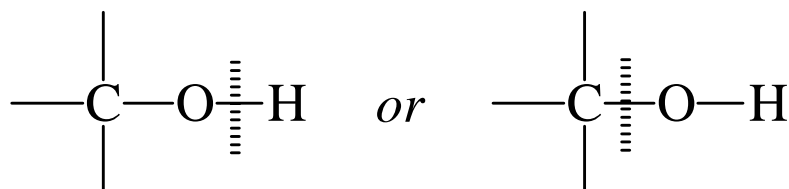


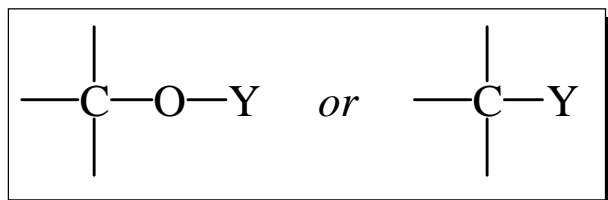
Alcohols: Reactions

The alcohol functional group is -O-H and its reactions involve cleavage of the O-H bond or the C-O bond —

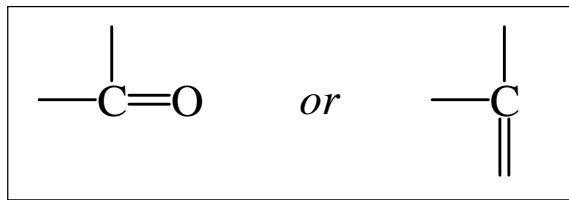


In either case, there can be a subsequent substitution, or an elimination to form a double bond ---

Substitution:

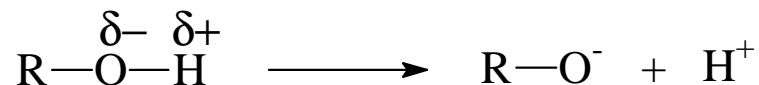


Elimination:

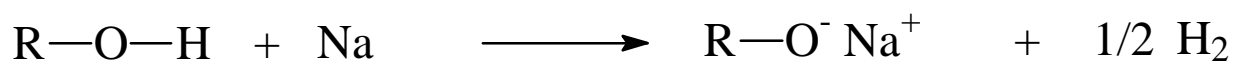


Alcohols As Acids —

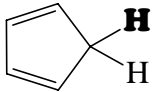

Acidity is the result of the electronegativity of oxygen:



Alcohols react with active metals:



Acidity of Alcohols, Compared to Other Compounds:

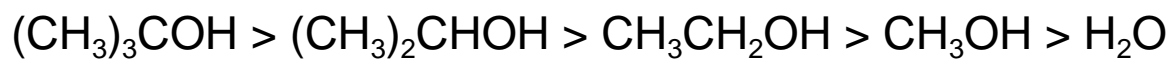
Compound	pK _a	Compound	pK _a
HSO₄H	-10	Ar OH	8-11
HCl	-7	HO H	15.74
ArSO ₃ H	-6.5		16
RCH ₂ -HO H ⁺	-2	RCH ₂ O H	18
H ₂ O H ⁺	-1.74	H-C≡C-H	25
HNO₃	-1.4	H ₂ N H	34
HF	3.17	CH ₂ =H H	36.5
Ar-H ₂ N H ⁺	3-5	Ph- H	37
RCOO H	4-5	CH ₃ -H ₂ C H	42
H ₃ N H ⁺	9		100

Relative Acidities of Alcohols and Water:

Compound	pK _a
HO- H	15.7
CH ₃ O- H	15.5-16
CH ₃ CH ₂ O- H	16-18
(CH ₃) ₂ CHO- H	18
(CH ₃) ₃ CO- H	19

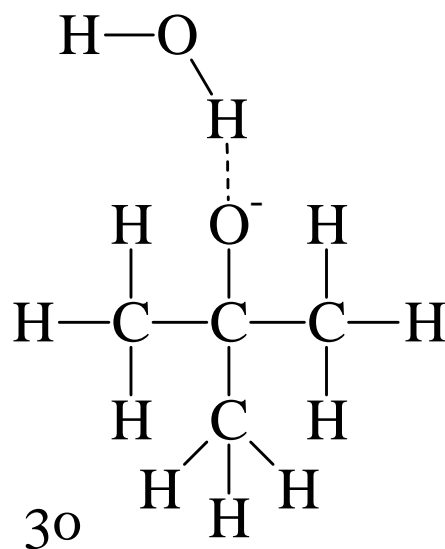
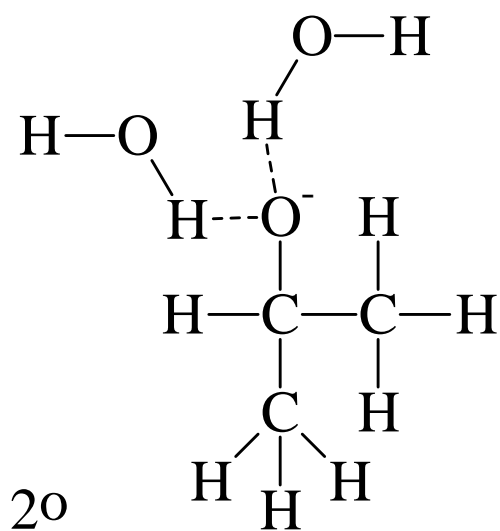
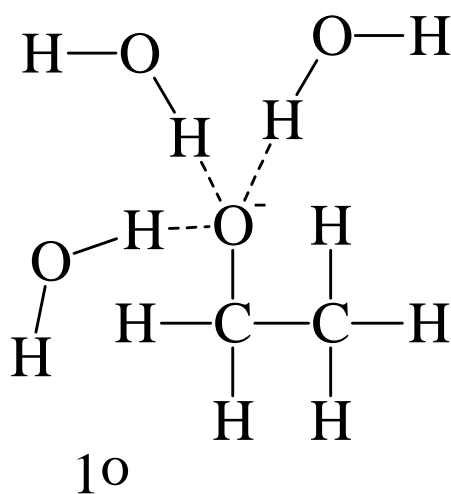
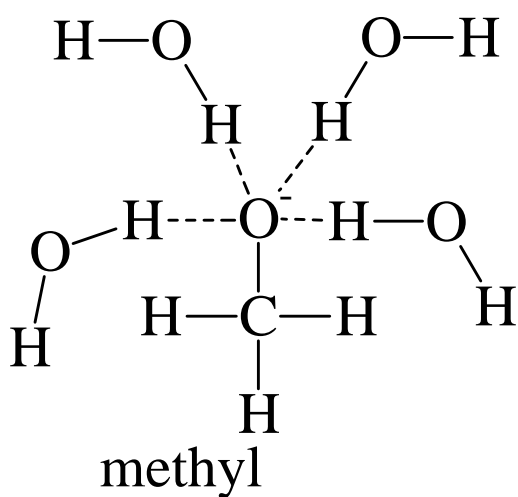
Is this order the result of destabilization of alkoxide anion by alkyl group electron releasing inductive effect?

Relative Gas Phase Acidities of Alcohols and Water:

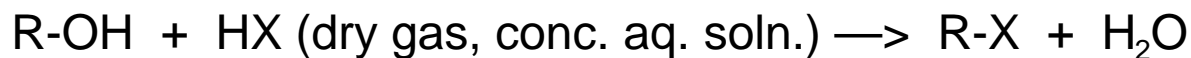


Explanation — Solvation of anions: $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$.

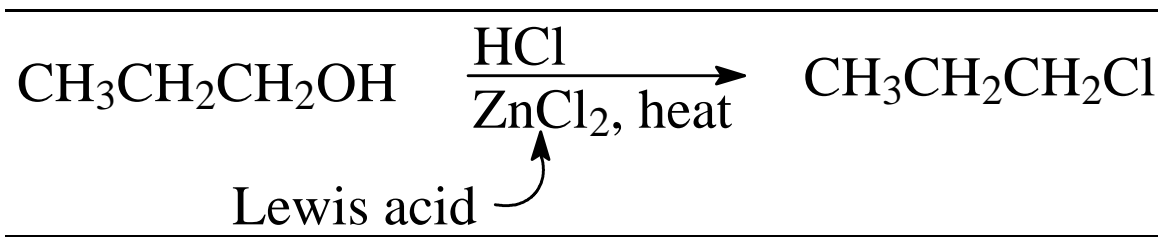
Alkoxide Anions Interact With Water



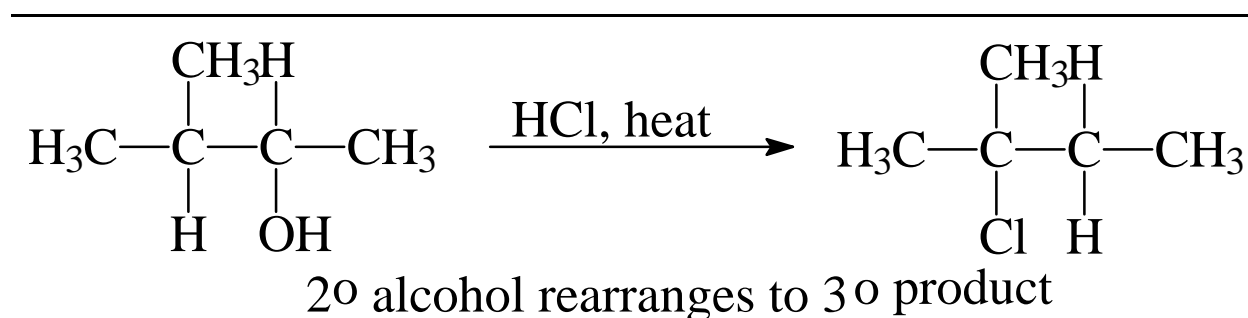
Reactions of Alcohols with H-X —



☞ acid catalyzed — eg addition of H_2SO_4 increases rate;
Lewis acids are also effective:



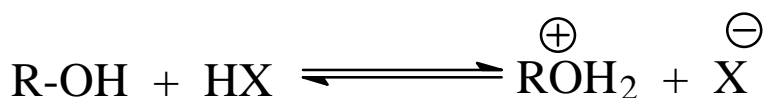
☞ The alkyl group may rearrange, except for most 1° alcohols:



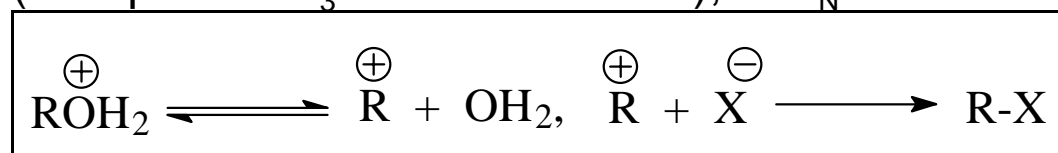
☞ Order of reactivity of R-OH:
benzyl, allyl $> 3^\circ > 2^\circ > 1^\circ < \text{CH}_3$.

Mechanism

Acid catalysis suggests protonation:



Rearrangement (except for 1° R-OH) and reactivity order (except for CH₃OH) suggest carbocation intermediates (except for CH₃OH and 1° R-OH), *ie* S_N1:



Most 1° alcohols and methanol, on the other hand, react via the S_N2 mechanism of the **protonated** alcohol (OH⁻ is a poor leaving group):



Summary ---

Generally S _N 1	Generally S _N 2
benzyl, allyl, 3°, 2°--- favored by formation of stable carbocation. S _N 2 disfavored for steric reasons for 3°, 2°.	1°, CH ₃ OH--- favored by steric reasons. S _N 1 disfavored owing to generation of unstable carbocation.

Tertiary alcohols

can be

converted into

halides by

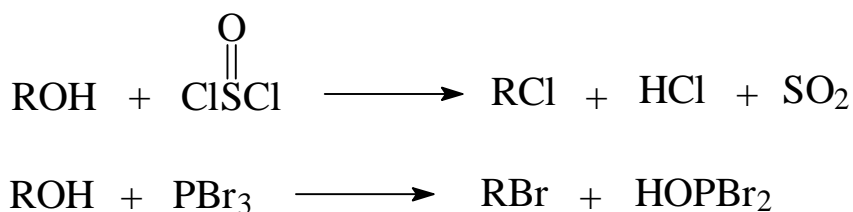
reaction with

HX. For primary

and secondary alcohols better results are often obtained

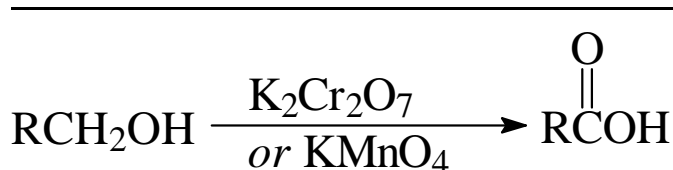
by reacting the alcohol with PBr_3 or SOCl_2 . These

reagents convert the $-\text{OH}$ into a good leaving group which is displaced by halide ion in an $\text{S}_{\text{N}}2$ reaction.



Oxidation of Alcohols ---

Primary alcohols can be oxidized to aldehydes (with care) and carboxylic acids.



Carboxylic Acids --- This oxidation occurs in two stages; there is an aldehyde intermediate,

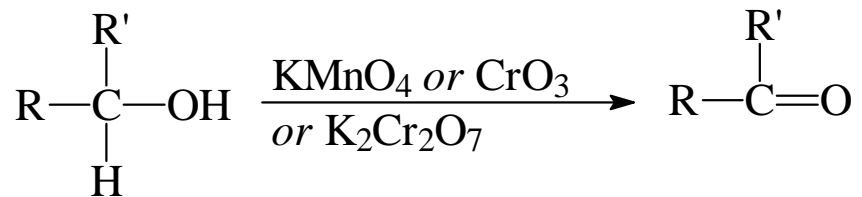
but aldehydes are usually more easily oxidized than alcohols (many aldehydes are oxidized by air) and under the conditions of the reaction the aldehyde is not isolated.

Aldehydes --- This reaction is successful under certain carefully controlled conditions.



$\text{C}_5\text{H}_5\text{NH}^+ \text{CrO}_3\text{Cl}^-$ is pyridinium chlorochromate, PCC

Secondary alcohols can be oxidized to ketones.



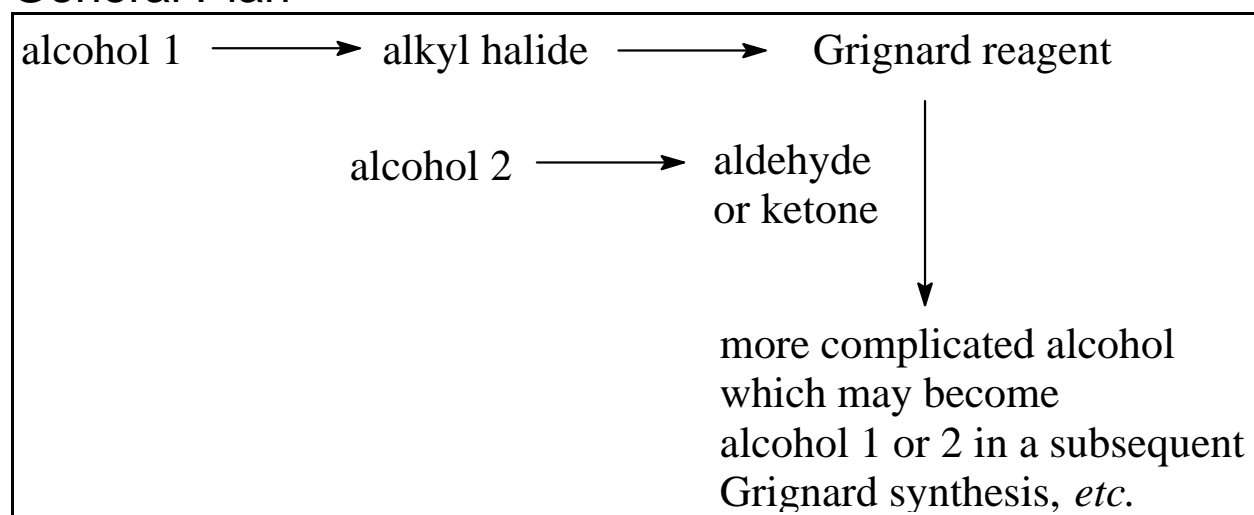
Further oxidation does not take place because it would involve

breaking a carbon-carbon bond.

Tertiary alcohols are not oxidized under basic conditions and are converted to alkenes under acidic conditions. [Alkenes may react with oxidizing agents.]

Grignard Synthesis of Alcohols

General Plan —



For example, starting with hydrocarbons or any aromatic compound containing 6 or fewer carbons synthesize the boxed compound below —

This step is possible because the order of reactivity of halides is $I > Br > Cl > F$ and alkyl halides are more reactive than aryl halides.

