

ALCOHOLS: Properties & Preparation

General formula: R-OH, where R is alkyl or substituted alkyl.

Ar-OH: phenol - different properties.

Nomenclature

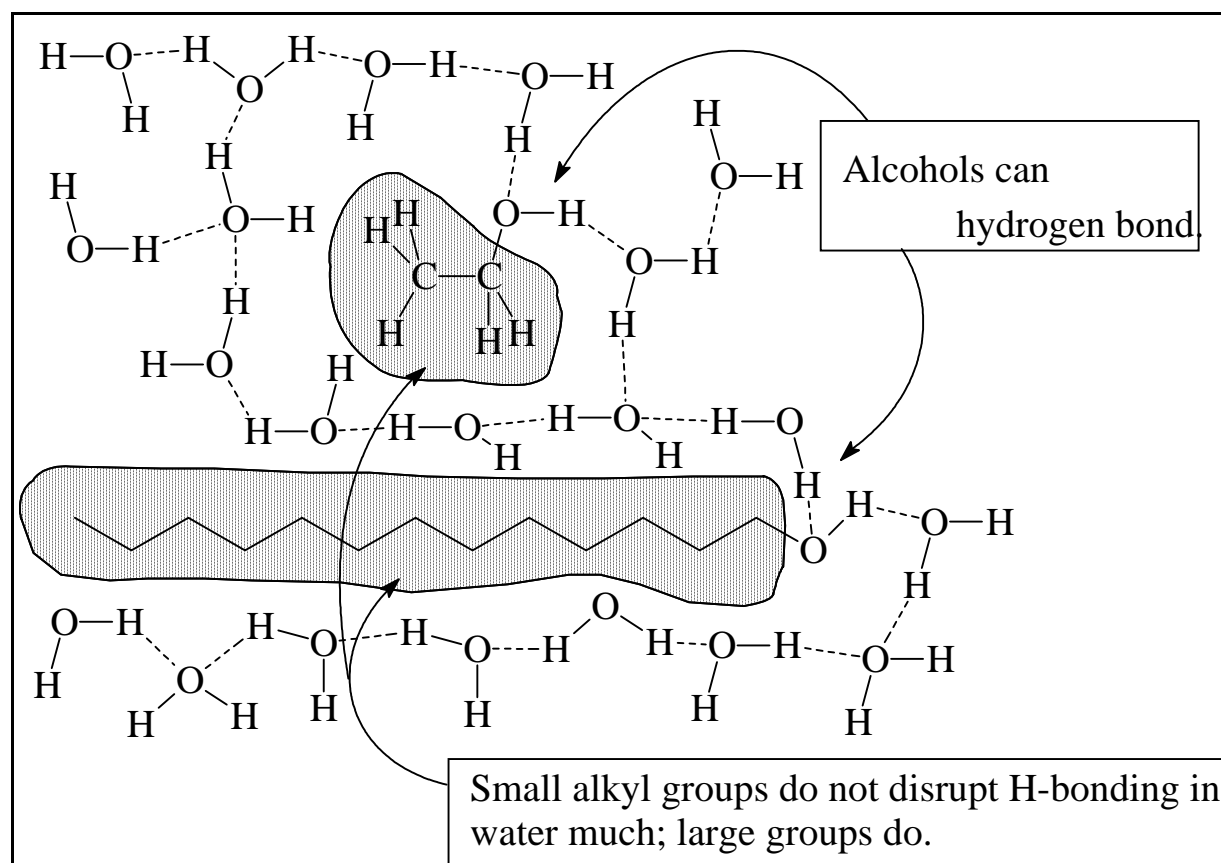
1. Common names: Name of alkyl group, followed by word alcohol.
2. Carbinol system: Alcohol is considered a derivative of CH₃OH. Name groups replacing methyl hydrogens, add the suffix carbinol.
3. IUPAC:
 - (a) Parent structure - longest chain containing -OH group: name by replacing -e of alkane by -ol
 - (b) Position of -OH is indicated by a number, usually the lowest one possible (-OH takes precedence over double and triple bonds if any are present, *ie*, number from the end that gives *the* -OH a lower number).
 - (c) Substituents on parent chain indicated by name and position number.
 - (d) More than one -OH group: -diol, -triol, *etc*.



3-chloro-4-phenyl-2-butanol

Physical Properties

Up to ~6 carbons: soluble in water owing to hydrogen bonding and dipole-dipole interactions with water. The larger the alkyl group, the more alkane-like the alcohol.



Owing to H-bonding and dipole-dipole interactions, the bps of alcohols are high compared to alkanes of same MW.

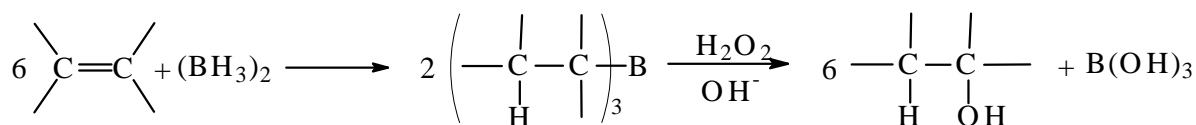
IR: Free O-H stretch (sharp) [not usually seen in neat liquid alcohol samples] at $\sim 3640\text{ cm}^{-1}$;

H-bonded O-H stretch (broad) $\sim 3350\text{ cm}^{-1}$

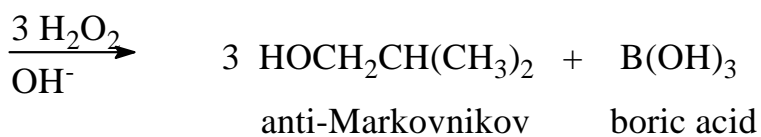
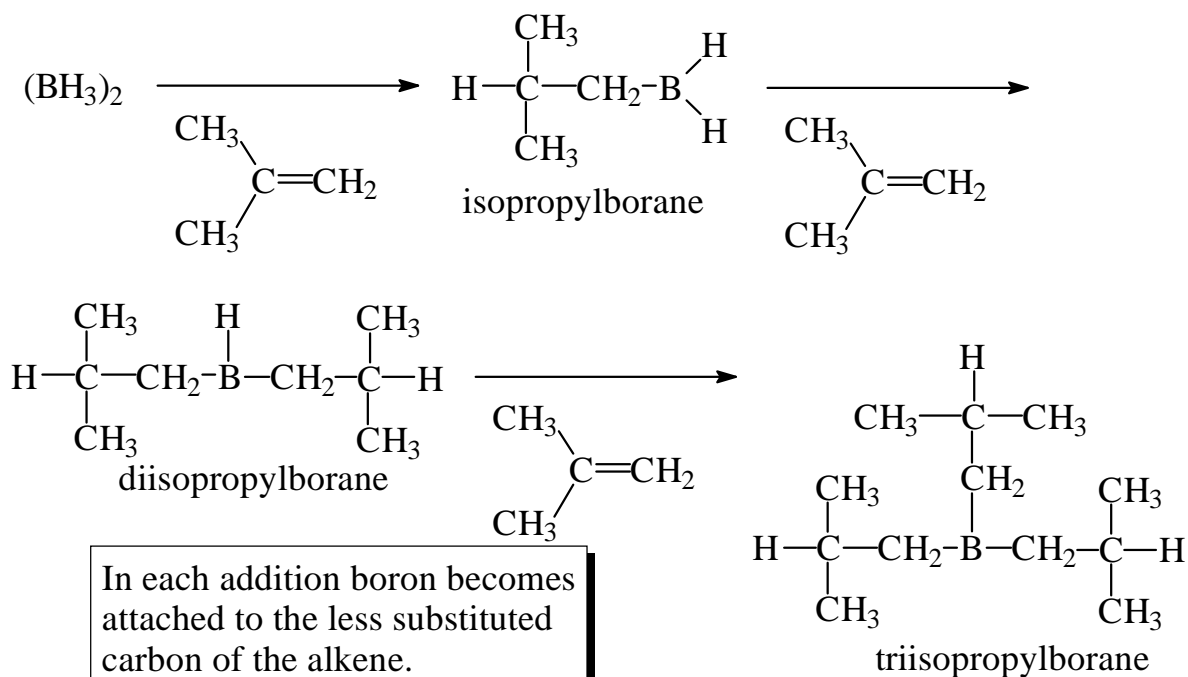
Preparation

1) Hydroboration-oxidation

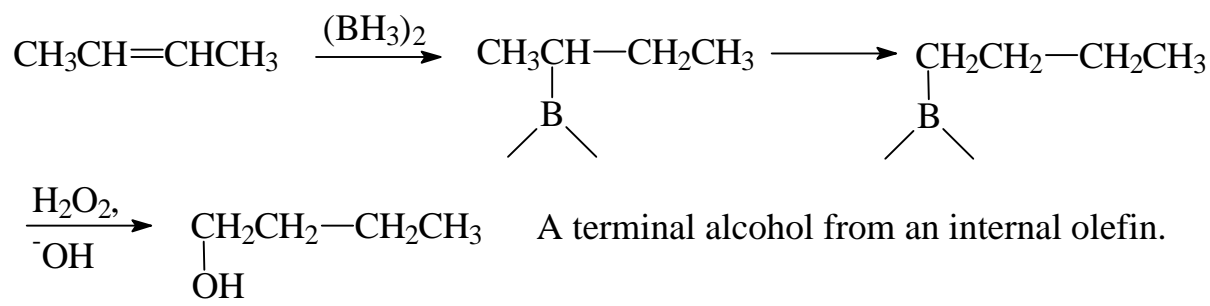
[Review Sect. 7.5, pgs. 231-34 in McMurry.] —



anti-Markovnikov, syn addition of H and OH w/o rearrangements, *eg*



If alkyl boranes are heated, they will isomerize to *terminal* alkylboranes *via* an elimination-readdition mechanism:



This can be a useful synthetic trick.

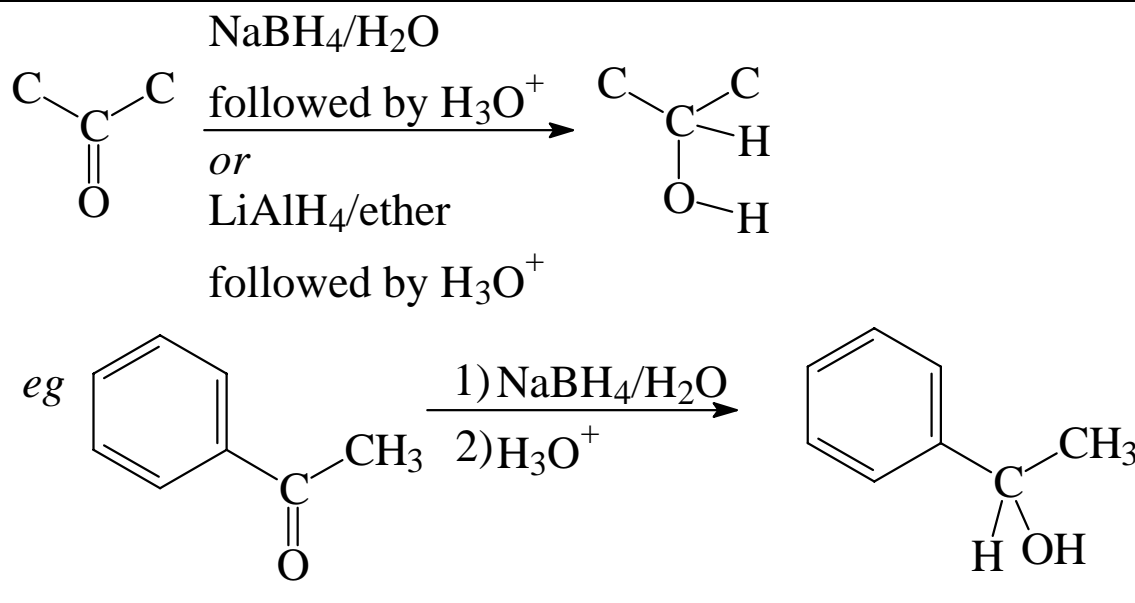
2) Hydration or Oxymercuration-Demercuration —

[Review Sect. 7.4, pgs. 228-31 in McMurry.]

Hydration of an alkene with water and a strong acid catalyst, or reaction of an alkene with $\text{Hg}(\text{OAc})_2$ in $\text{H}_2\text{O}/\text{THF}$ followed by NaBH_4 , leads to Markovnikov addition. In the case of mercuriation the addition shows anti stereochemistry.

3) Reduction of Ketones ---

Ketones can be reduced to secondary alcohols with lithium aluminum hydride or sodium borohydride.



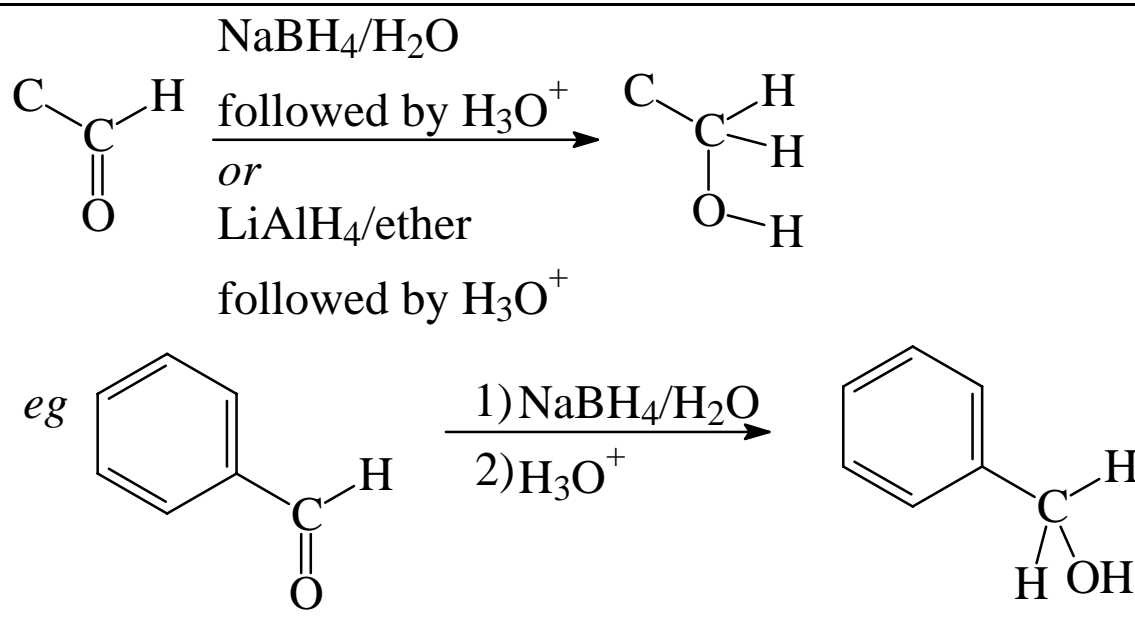
Limitations —

Sodium borohydride may reduce the C-C π bond in conjugated ketones.

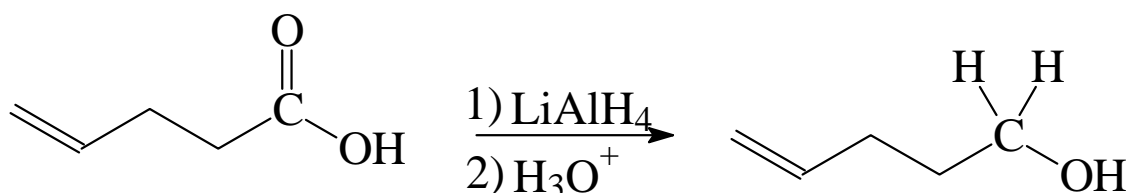
Lithium aluminum hydride is a powerful reducing agent and will reduce carboxylic acids, esters, nitriles, amides and nitro groups; it will replace alkyl halogens with hydrogen (*hydrogenolysis*). It is destroyed by even weakly acidic water and alcohols. It may reduce the C-C π bond in conjugated ketones. It reacts violently with water and, in general, is nasty stuff.

4) Reduction of Aldehydes —

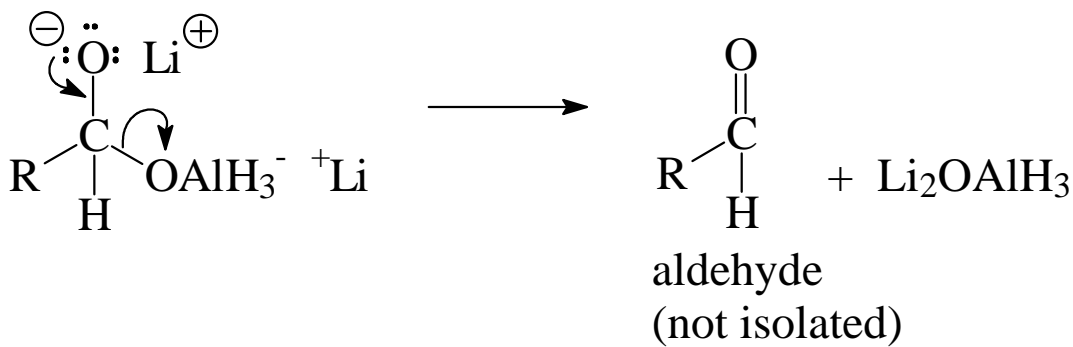
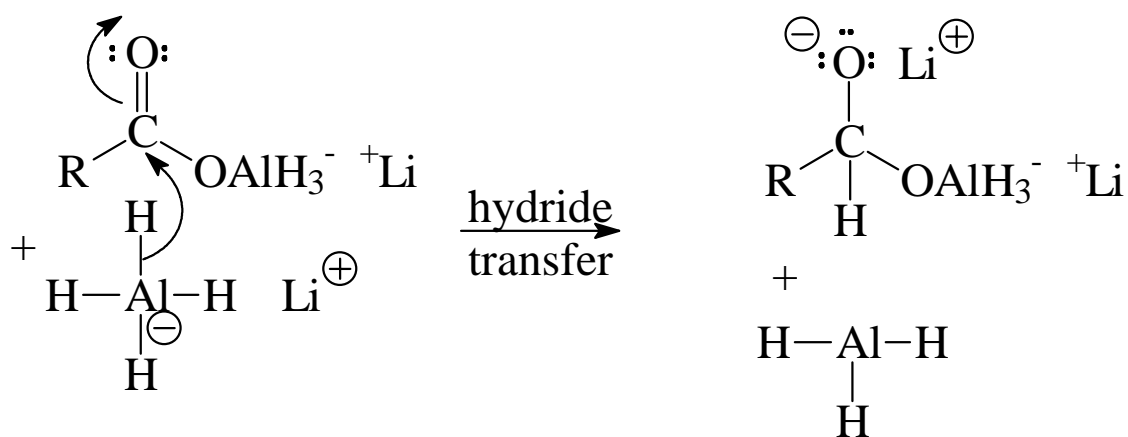
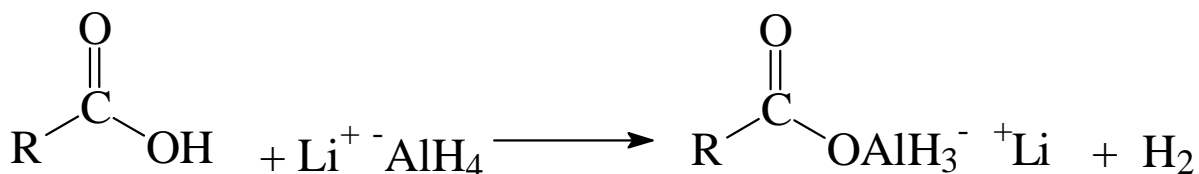
Aldehydes can be reduced to primary alcohols with sodium borohydride or lithium aluminum hydride. This reaction is analogous to (3).

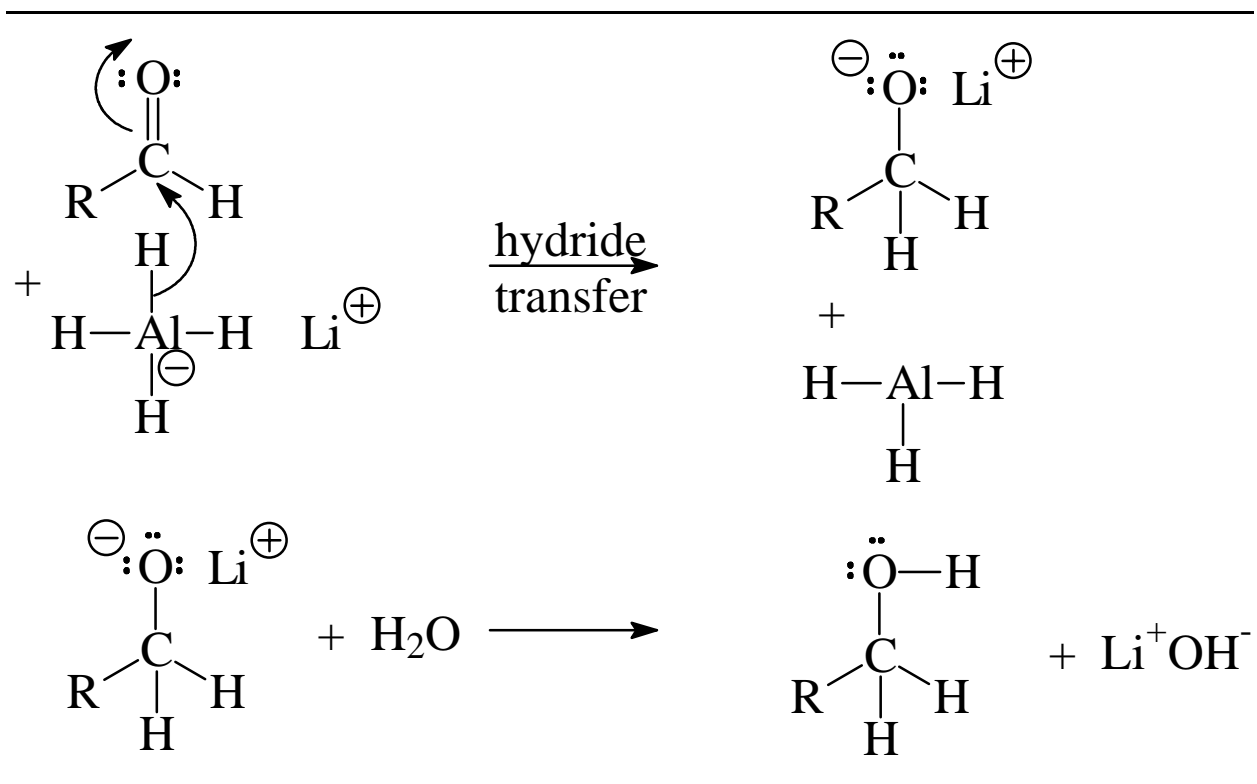


5) Reduction of Carboxylic Acids and Esters —
 Esters can be reduced to primary alcohols, $R-CO-O-R' \rightarrow R-CH_2-OH + H-O-R'$, by sodium metal in ethanol (the Bouveault-Blanc reduction). Both esters and carboxylic acids can be reduced to primary alcohols by lithium aluminum hydride.



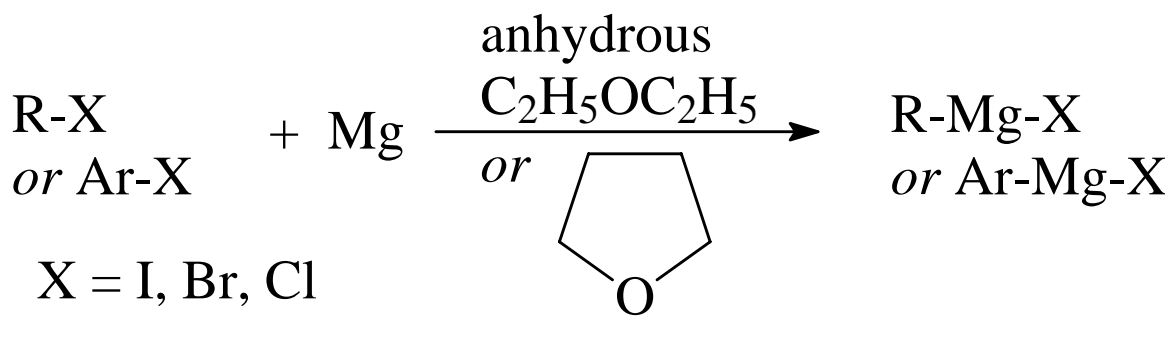
via (simplified):



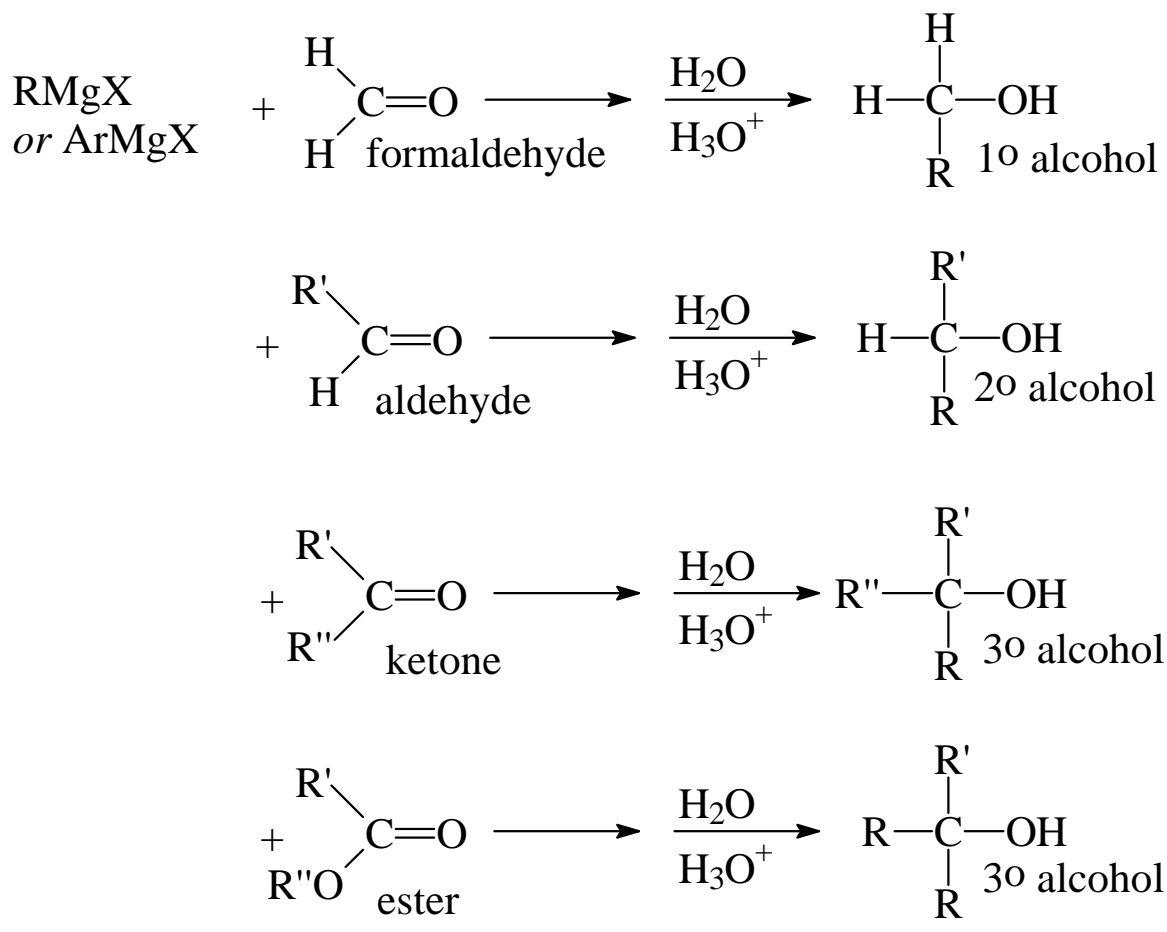


Note the unusual *hydride* (H^-) transfers in the above mechanism. This is different from the common proton (H^+) transfers we see in Bronsted-Lowry acid-base reactions.

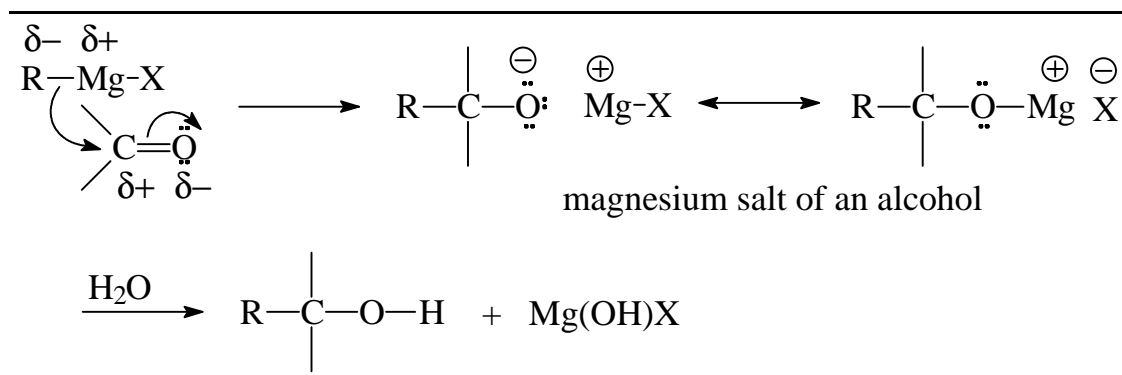
6) Grignard Synthesis (Smaller \rightarrow Larger)
 Formation of Grignard reagent —



Grignards react with aldehydes, ketones, and esters to give alcohols —

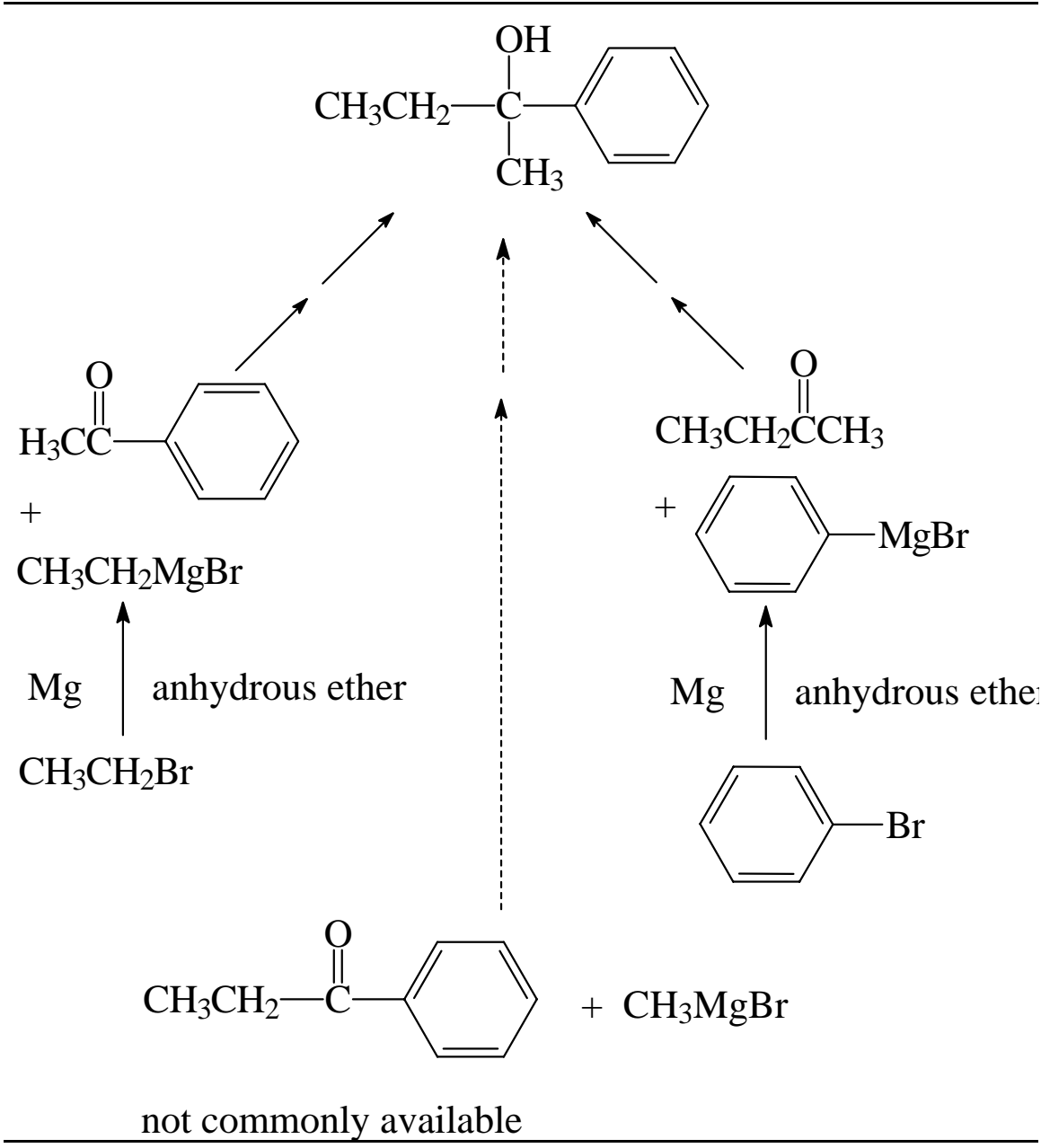


Pseudomechanism —



Synthesize 2-phenyl-2-butanol using a Grignard synthesis —

The figure below shows three possible routes by which this synthesis can be accomplished. In practice, the route chosen would likely depend on the starting materials that may be at hand in the laboratory (all of these compounds could be purchased).



CH_3MgBr could be made from CH_3Br and Mg , but methyl bromide is not convenient to handle. It boils at 4°C , so it is a gas at room temperature. [Large quantities of methyl chloride are used as a soil and grain fumigant. Its use is quite controversial since it is somewhat toxic and an ozone depleting chemical. See, for example: <http://www.epa.gov/docs/ozone/mbr/mbrqa.html>]