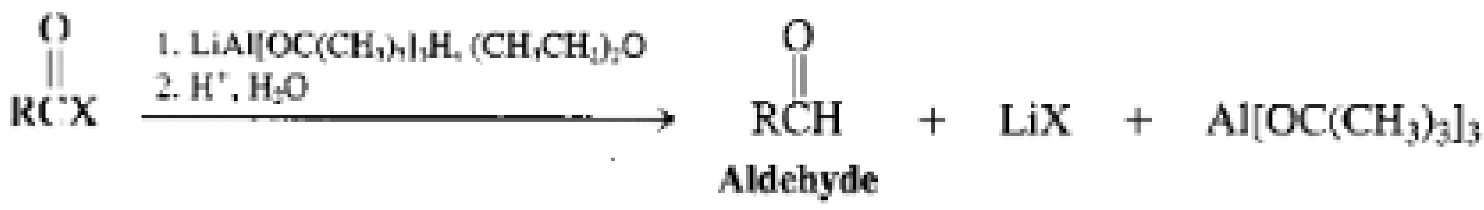
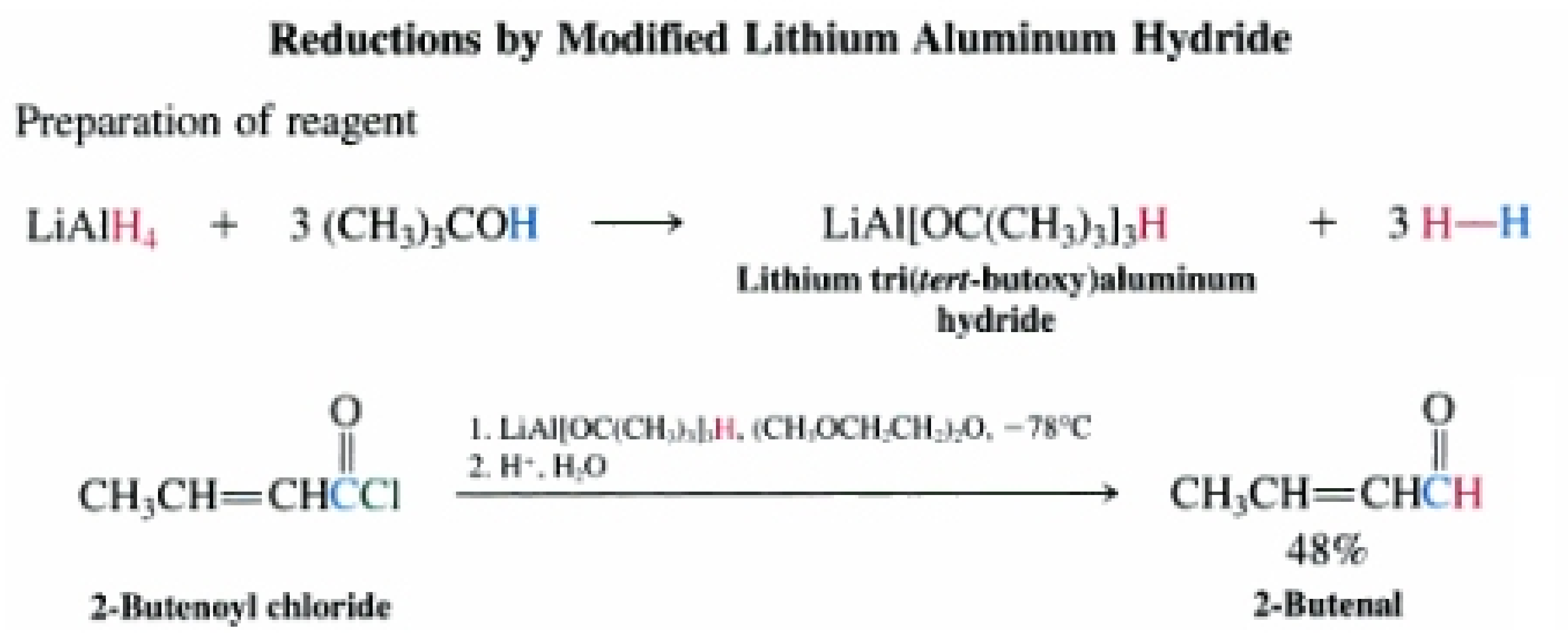
Acyl Halides + Hydrides (Hydride Reduction)



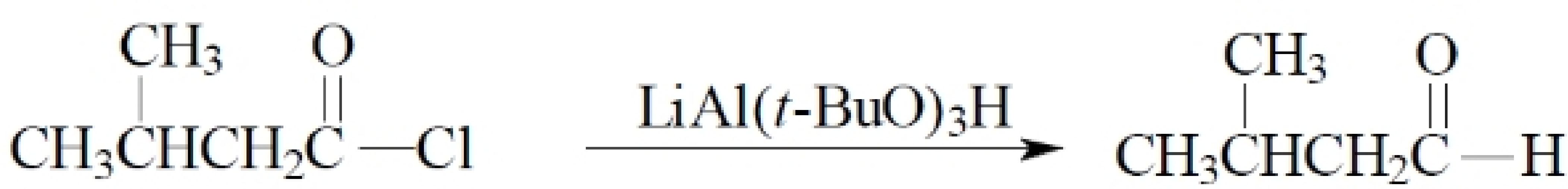
Lithium aluminum hydride ($LiAlH_4$) reduces acyl halides to primary alcohols; acyl halides with react with a weaker reducing agent to yield an aldehyde.

We can convert an acyl chloride into an aldehyde by hydride reduction. In this transformation, we face a selectivity problem: lithium aluminum hydride ($LiAlH_4$) and sodium borohydride reduce acyl halides to alcohols.

To prevent such overreduction, we must modify $LiAlH_4$ by letting it first react with three molecules of 2-methyl-2-propanol (*tert*-butyl alcohol). This treatment neutralizes three of the reactive hydride atoms, leaving one behind that is nucleophilic enough to attack an acyl chloride by not the resulting aldehyde.

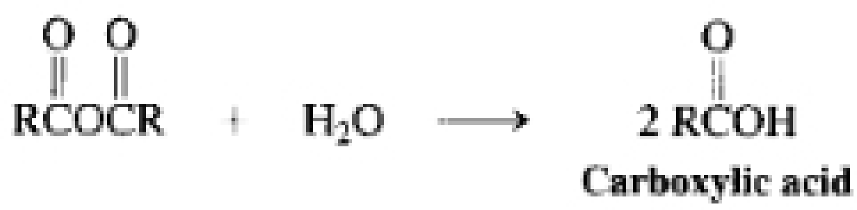


Example:



Reactions of Carboxylic Acid Anhydrides

Carboxylic Acid Anhydrides + Water



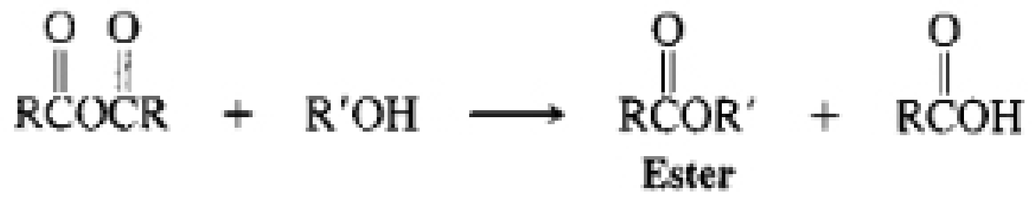
Hydrolysis occurs quickly, even in moist air with no acid or base catalyst.

Reagents must be protected from moisture.

In every addition-elimination reaction *except hydrolysis*, the carboxylic acid side product is usually undesired and is removed by work-up with aqueous base.

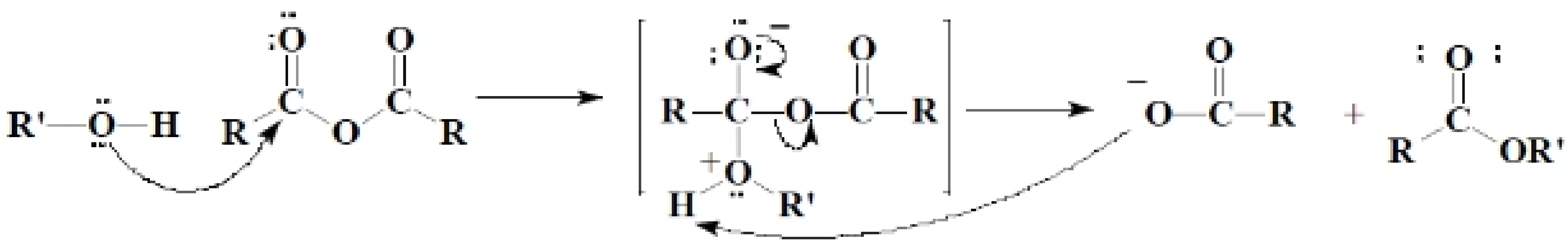
Reactions of Carboxylic Acid Anhydrides

Carboxylic Acid Anhydrides + Alcohols



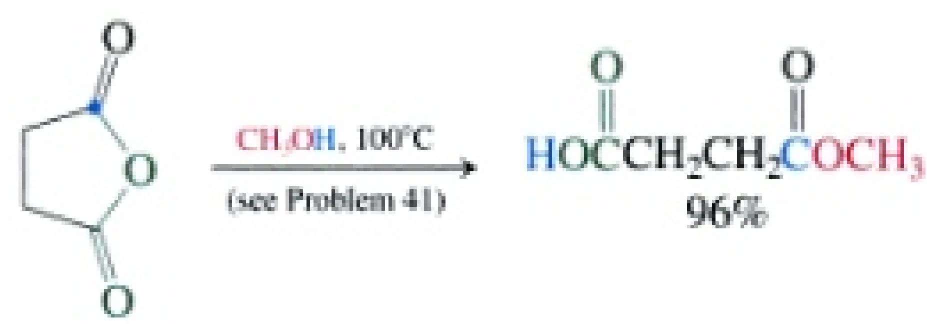
MECHANISM:

- Alcohol attacks one C=O of anhydride.
- Tetrahedral intermediate forms.
- Carboxylate ion leaves, C=O is restored, H^+ is abstracted.



Cyclic anhydrides undergo similar nucleophilic addition-elimination reactions that lead to ring opening.

Nucleophilic Ring Opening of Cyclic Anhydrides



Butanedioic (succinic) anhydride