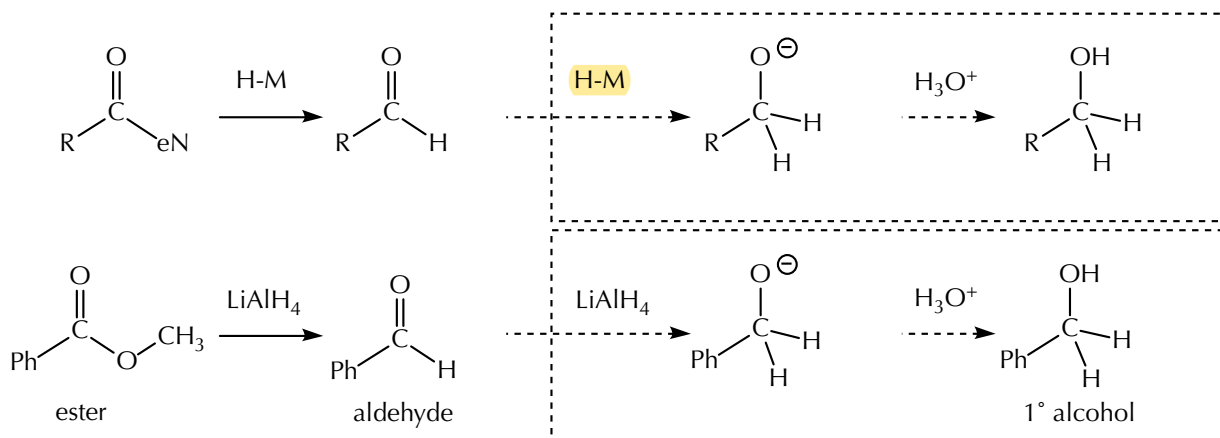


Figure 1311

Structural relationships in acylation reactions using hydride nucleophiles.



The acylation product of a hydride nucleophile is an aldehyde.

As with the ketones in the previous section, the further addition reactions of aldehydes with nucleophilic hydrides are also familiar from Chapter 12.

The reaction between the ester, methyl benzoate, and lithium aluminum hydride gives benzaldehyde. Also as in the previous section, the carbonyl group from this acylation reaction product (the aldehyde) is more reactive towards the hydride reagent than towards the resonance-stabilized carbonyl group of the starting material (the ester). The second reaction (addition of hydride to the aldehyde) takes place faster than the first one (acylation of hydride by the ester). Excess of the hydride reagent is the normal reaction procedure, resulting in the formation of the primary alcohol as the observed product.

A final reminder about the outline of this chapter. The presentation in this first section was meant to establish the structural relationship that all acylation reactions have in common, namely, substitution at the sp^2 carbon of a carbonyl group of a carboxylic acid or an acid derivative. The acylation reaction concept extends to other functional groups that are structural analogies to acyl groups, such as those with carbon-nitrogen double bonds.

You are strongly recommended to do the first set of Practice Questions (13.01–13.04), with an eye on seeing the common bonding pattern for acylation reactions, before going in deeper with the details of the reaction mechanisms in Section 13.2.