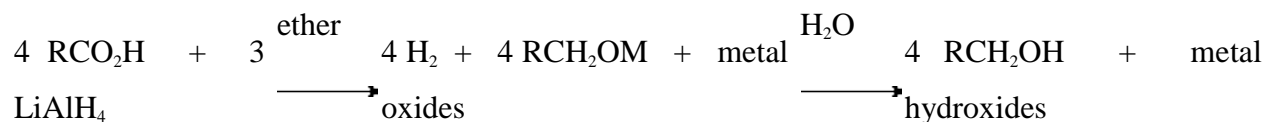


Reductions and Oxidations of Carboxylic Acids

1. Reduction

The carbon atom of a carboxyl group is in a relatively high oxidation state. Reduction to a 1°-alcohol takes place rapidly on treatment with the powerful metal hydride reagent, lithium aluminum hydride, as shown by the following equation. One third of the hydride is lost as hydrogen gas, and the initial product consists of metal salts which must be hydrolyzed to generate the alcohol. These reductions take place by the addition of hydride to the carbonyl carbon, in the same manner noted earlier for aldehydes and ketones. The resulting salt of a carbonyl hydrate then breaks down to an aldehyde that undergoes further reduction.

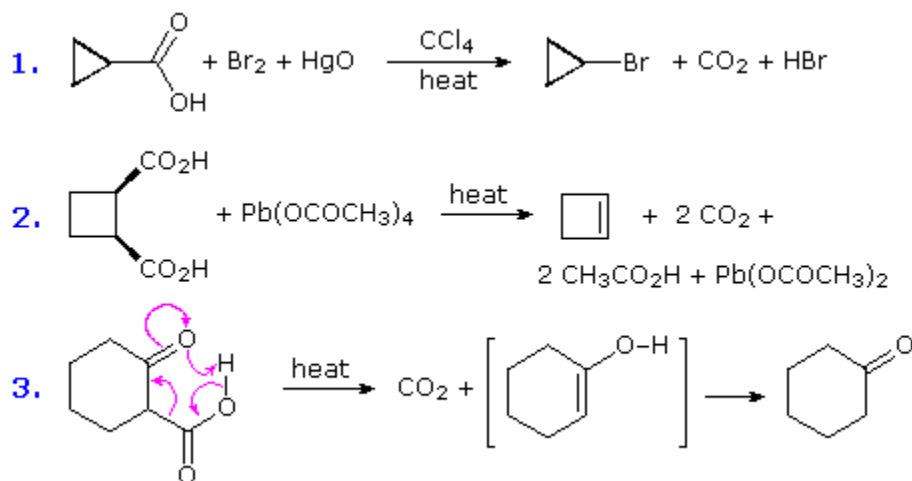


Diborane, B₂H₆, reduces the carboxyl group in a similar fashion. Sodium borohydride, NaBH₄, does not reduce carboxylic acids; however, hydrogen gas is liberated and salts of the acid are formed. Partial reduction of carboxylic acids directly to aldehydes is not possible, but such conversions have been achieved in two steps by way of certain carboxyl derivatives. These will be described later.

2. Oxidation

Because it is already in a high oxidation state, further oxidation removes the carboxyl carbon as carbon dioxide. Depending on the reaction conditions, the oxidation state of the remaining organic structure may be higher, lower or unchanged. The following reactions are all examples of **decarboxylation** (loss of CO₂). In the first, bromine replaces the carboxyl group, so both the carboxyl carbon atom and the remaining

organic moiety are oxidized. Silver salts have also been used to initiate this transformation, which is known as the **Hunsdiecker reaction**. The second reaction is an interesting bis-decarboxylation, in which the atoms of the organic residue retain their original oxidation states. Lead tetraacetate will also oxidize mono-carboxylic acids in a manner similar to reaction #1. Finally, the third example illustrates the general decarboxylation of β -keto acids, which leaves the organic residue in a reduced state (note that the CO_2 carbon has increased its oxidation state.).



Three additional examples of the Hunsdiecker reaction and a proposed mechanism for the transformation will be shown above by clicking on the diagram. Note that the meta-dihalobenzene formed in reaction 4 could not be made by direct halogenation reactions, since chlorine and bromine are ortho/para-directing substituents. Also, various iodide derivatives may be prepared directly from the corresponding carboxylic acids. A heavy metal carboxylate salt is transformed into an acyl hypohalide by the action of a halogen. The weak oxygen-halogen bond in this intermediate cleaves homolytically when heated or exposed to light, and the resulting carboxy radical decarboxylates to an alkyl or aryl radical. A chain reaction then repeats these events. Since acyl hypohalites are a source of electrophilic halogen, this reaction takes a different course when double bonds and reactive benzene derivatives are present. In this respect remember the addition of hypohalous reagents to double bonds and the facile bromination of anisole.