Tin catalyzed reaction of trioses with alcohols to give alkyl lactates

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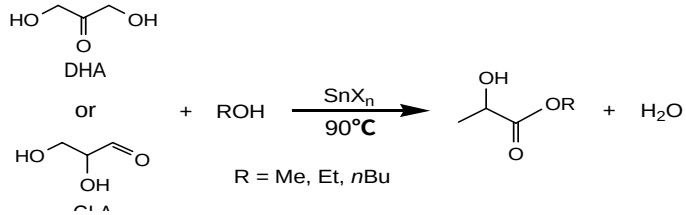
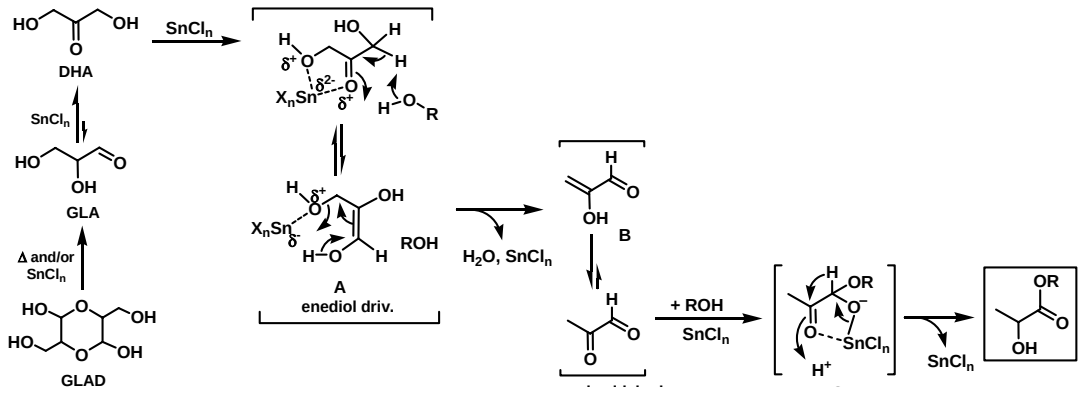
In order for the biodiesel fuel (BDF) production to be economically viable, its major by-product, glycerol should be used effectively. It has been known that it can be partially oxidized to dihydroxyacetone (DHA),[1] which in turn can be converted to alkyl lactates by the reaction with alcohols in the presence of zirconium or chromium catalyst.[2] We investigated this reaction and found that tin halides can be an excellent catalyst for the reaction of dihydroxyacetone as well as glyceraldehyde (GLA) to give alkyl lactates in higher yields even under milder reaction conditions.



Among the several tin compounds examined, $SnCl_2$ and $SnCl_4 \cdot 5H_2O$ could promote smooth conversions of DHA and GLA to methyl lactate in yields up to 80 ~ 90%. These tin chlorides were not inactivated after the reaction, and allowed repeatedly added trioses at least 5 times to be converted to methyl lactate over 80% yield.

In an estimated reaction mechanism, DHA may strongly interact with $SnCl_n$ to give a cyclic intermediate containing Sn---OH and Sn---O=C bonds, whose isomerization to its enediol derivative may be promoted by the presence of ROH (Scheme 2, **A**). The enediol form **A** would give rise to enol-pyruvic aldehyde (Scheme 2, **B**), which may be immediately isomerized to pyruvic aldehyde. Again $SnCl_n$ might strongly coordinate to this compound to form a specific intermediate as **C** (Scheme 2), which can cause a 1,2-hydride shift from the terminal carbon to the central one to predominantly yield alkyl lactate.



1 Japanese Patent 2875634 (for Kao).

2 EU Patent 0 460 831 A2, 1991 and EU Patent 0 541 330 A2, 1992 (for BP).